Olefins from Thermal Decomposition of *N*-Sulfoximino-2-oxazolidones. A Novel Synthesis of Bicyclo[3.3.1]non-1-ene

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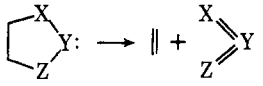
Abstract: 3-Amino-2-oxazolidones (**7a–g**) were prepared stereospecifically by condensation of 2-hydroxyalkylhydrazines (obtained by hydrazinolysis of the corresponding epoxides) with diethyl carbonate in the presence of sodium methoxide or by N-amination of a 2-oxazolidone (**7a,e,h–j**). The appropriate oxazolidone was prepared either by condensation of a 2-hydroxyalkylamine, obtained by ammonolysis of an epoxide, with phosgene (**10a**) or *N,N'*-carbonyldiimidazole (**10b**), or by nitrosation of a β-hydroxycarbohydrazide (**13**). Oxidation of 3-amino-2-oxazolidones with lead tetraacetate in Me_2SO gave the 3-sulfoximino derivatives **14a–j.** Except for **14h,** these sulfoximines underwent smooth pyrolysis at <140 °C to yield Me_2SO, CO_2, N_2, and an olefin. The latter was shown to be formed via a syn elimination from the sulfoximine **14,** probably involving the diazene **4** as an intermediate. Application of this olefin synthesis to a preparation of bicyclo[3.3.1]non-1-ene led from keto ester **16** to exo sulfoximine **24** which, by a syn elimination, gave *Z* isomer **15a** in an isolated 53% yield. Synthesis of endo sulfoximine **28,** followed by pyrolysis (150 °C), afforded carboxylic acid **28.** The latter is believed to be formed via the highly strained *E*-bicyclo[3.3.1]non-1-ene (**15b**), which is trapped by extruded CO_2.

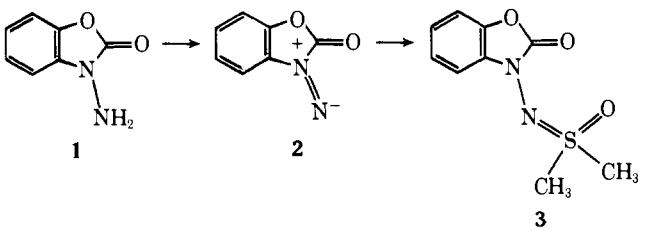
The formation of olefins by cyclic elimination processes, eq 1, has become a well-established method of synthesis for this



(1)

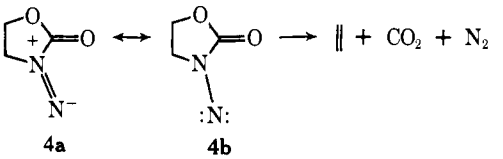
functional group.[1] Cheletropic reactions[2] involving thionocarbonates,[3,4] epoxides,[5] aziridines,[6] episulfides,[7] episelenides,[8] β-lactones,[9] pyrrolidines,[10] 2-phenyldioxolidines,[11] and certain, cyclic azo compounds,[12] have been used as a means of access to olefins. A characteristic feature of these extrusion processes is their generally large exothermicity, and this factor, in combination with orbital symmetry constraints, probably contributes heavily to the high degree of stereoselectivity observed in olefin formation by this method. The objective of this work was the development of an olefin synthesis which, in addition to possessing the efficiency, regiospecificity, and stereospecificity associated with alternative methods, could also be carried out under mild conditions and without contamination from by-products. It was intended that this synthesis be applicable to both highly strained and exceptionally sensitive double bonds, so that the use of acidic or basic reagents in the elimination process was precluded. A thermal or photochemical cycloelimination of low activation energy appeared ideal.

A study by Rees and Atkinson,[13] in which the *N*-amino derivative **1** of benzooxazolinone was shown to undergo oxidation with lead tetraacetate to diazene **2,** suggested a potentially useful heterocyclic system with many of the attributes we desired. Although **2** did not undergo cycloreversion to benzyne, carbon dioxide and nitrogen, as had been hoped, it seemed likely that elimination from the nonannelated diazene **4** should be appreciably more exothermic; this system was therefore selected as the focus for study in the hope of realizing the chemistry depicted in Scheme I.[14]



1 **2** **3**

Scheme I

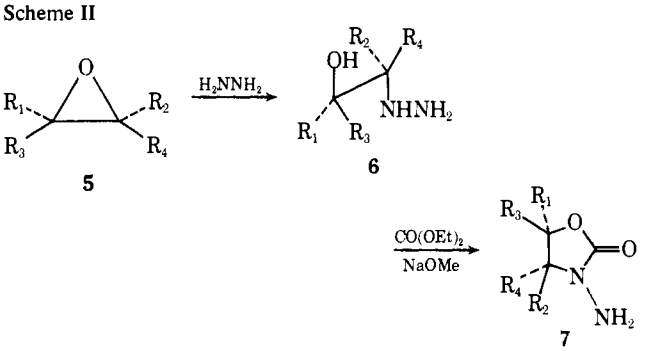


4a **4b**

Diazenes are known to be unstable species,[15] with the terminal nitrogen strongly electrophilic. This property, which presumably reflects a major contribution from the nitrene resonance form **4b,** is manifest in the reaction of **2** with Me_2SO to give the sulfoximine **3.**[16] The diazene **2** is known to be regenerated from **3** upon photolysis.[17]

Preparation of Sulfoximines of 3-Amino-2-oxazolidones. Condensation of vicinal hydroxyhydrazines (e.g., **6**) with diethyl carbonate in the presence of sodium methoxide has been shown to afford 3-amino-2-oxazolidones **7** (Scheme II).[19] In practice, yields of substituted aminooxazolidones prepared by this route are quite low (see Table I) due, in part, to the further condensation of **7** with diethyl carbonate to give a urethane. A modification of the procedure of Evans and Jones[18] permitted the isolation of crystalline aminooxazolidones in most cases, without the need for purification. Compounds of type **7** showed carbonyl absorption at ca. 1745 cm^{-1}, as well as the typical absorption of a primary amine (two bands) at ca. 3300 cm^{-1}.

Scheme II



5 **6** **7**

The required hydrazines **6a–g** were obtained by treatment of the appropriate epoxide **5** with hydrazine hydrate and, in accord with earlier results,[20] gave products from a highly regioselective attack. The one exception, that of *cis*-2-pentene

Table 1. 3-Amino-2-oxazolidones (**7**) and 3-Sulfoximino-2-oxazolidones (**14**)

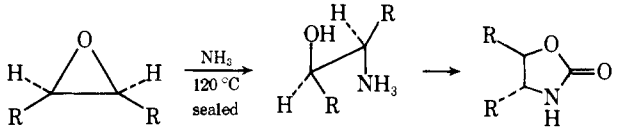
				7				14		
R_1	R_2	R_3	R_4	Compd	Method of prep[a]	Mp, °C	Yield, %	Compd	Mp, °C[b]	Yield, %
H	H	H	H	**7a**	A	70–71	60	**14a**	118–120	68
					B		38			
CH_3	H	H	H	**7b**	A	oil	63	**14b**	109	58
C_6H_5	H	H	H	**7c**	A	102–103	16	**14c**	131–135	78
C_6H_5	H	H	C_6H_5	**7d**	A	140–142	31	**14d**	190–195	79
$-(CH_2)_6-$		H	H	**7e**	A	oil	21	**14e**	123–125	68
					B		12			
CH_3	C_2H_5	H	H	**7f**	A	oil	46	**14f**[c]	oil	67
C_2H_5	CH_3	H	H	**7g**				**14g**		
Benzo				**7h**	B	169–170	81	**14h**	174–175	68
C_6H_5	C_6H_5	H	H	**7i**	B	110–112	28	[**14i**][d]		
$-(CH_2)_4-$	H		H	**7j**	B	92–95	39	**14j**	124	77

[a] Method A: $RR'C(OH)CR''R'''NHNH_2/CO(OEt)_2/NaOMe$. Method B: 2-Oxazolidone/2,4-$(NO_2)_2C_6H_3ONH_2$/BuLi. [b] Melting is accompanied by abrupt decomposition with gas evolution. [c] A 1:1 mixture of these two compounds was obtained. [d] Not isolated.

epoxide, not unexpectedly gave an approximately 1:1 mixture of hydrazines, and hence a mixture of **7f** and **7g**. The opening of *cis*-cyclooctene oxide[21] with hydrazine required forcing conditions[22] but, nevertheless, gave *trans*-2-hydroxycyclooctylhydrazine in excellent yield. A consequence of trans opening of the epoxide **5**, followed by cyclization of **6** to **7** without change in configuration, is that stereochemistry is inverted between **5** (and consequently the olefin from which it derives) and aminooxazolidone **7**. Obtention of a single stereoisomer in each case was verified by straightforward analysis of NMR resonances due to the readily distinguishable protons on carbon adjacent to oxygen and to nitrogen.

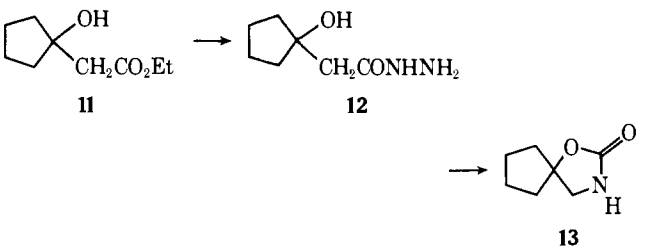
An alternative route (Scheme III) to the 3-amino-2-oxazolidone system was investigated, based upon functionalization at nitrogen of the readily available oxazolidone precursor. *trans*-4,5-Diphenyl-2-oxazolidone (**10a**) was prepared in 83% yield by condensation of the threo amino alcohol **9a**,[23] obtained from *cis*-stilbene oxide (**8a**) and ammonia, with phosgene;[24] the more sensitive, trans-fused cyclooctyloxazolidone **10b** was conveniently made from **9b**[22] in 52% yield by treatment with *N,N'*-carbonyldiimidazole in THF. For preparation of spirooxazolidone **13**, the method of Newman,[25] involving diazotization of a β-hydroxycarbohydrazide, was adopted (Scheme IV). Thus, β-hydroxy ester **11**, prepared by a modified Reformatsky reaction,[26] was converted in 82% yield to hydrazide **12**, and the latter was treated with nitrous acid. The resulting acyl azide underwent spontaneous Curtius rearrangement, with internal trapping of the isocyanate formed, to produce **13** in 79% yield.

Scheme III



8a, R = C_6H_5 **9a**, R = C_6H_5 **10a**, R = C_6H_5
8b, R = $-(CH_2)_6-$ **9b**, R = $-(CH_2)_6-$ **10b**, R = $-(CH_2)_6-$

Scheme IV

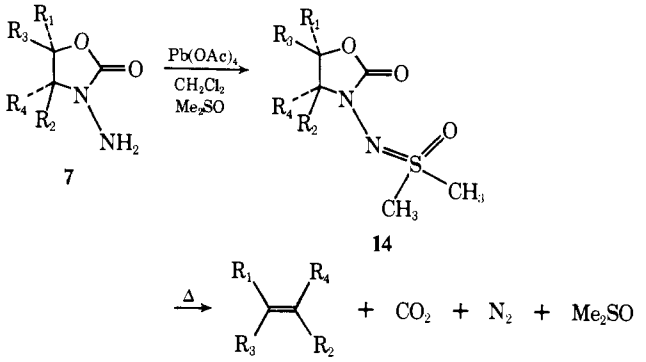


11 **12** **13**

Initial attempts to introduce the *N*-amino function into oxazolidones **10a**, **10b**, and **13** were made via the corresponding *N*-nitroso derivatives.[24] Although nitrosation of, for example, **13** proceeded normally, the product behaved quite differently from the *N*-nitroso derivative of a typical secondary amide.[27] Under a variety of reducing conditions including hydrogenation, the *N*-nitrosooxazolidone is converted in near quantitative yield to **13**. The introduction of amine functions by direct amination has been successful in certain instances,[28] and it was found that treatment of benzo-2-oxazolidone with butyllithium, followed by *O*-(2,4-dinitrophenyl)hydroxylamine,[29] gave **7h** in excellent yield. Application of this method to nonannelated oxazolidones, unfortunately, gave lower yields of the corresponding amino derivatives (Table I, method B). Other aminating agents such as hydroxylamine-*O*-sulfonate, although effective in the case of **7h**,[13] gave negligible yields of other aminooxazolidones.

Oxidation of the 3-amino-2-oxazolidones **7a–j**, with trapping as the corresponding sulfoximino derivatives **14a–j** (see Table I), was carried out with lead tetraacetate in a mixture of dichloromethane and dimethyl sulfoxide (Scheme V).[17] The resulting sulfoximines are colorless, crystalline substances, which are stable in the solid state. In solution they undergo rapid decomposition at temperatures >90 °C, with brisk gas evolution (vide infra). The carbonyl absorption of sulfoximines of type **14** is shifted to slightly higher frequency (ca. 1760 cm^{-1}), compared with the aminooxazolidone progenitor. The proton signals of methyl groups bound to sulfur in these sulfoximines are significantly downfield (at ca. δ 3.2) from the corresponding methyl protons in dimethyl sulfoxide and, in all except the parent **14a**, the methyl groups are magnetically nonequivalent. This latter feature is consistent with the absence

Scheme V



7 **14**

$\xrightarrow{\Delta}$ + CO_2 + N_2 + Me_2SO

of rotation about S-N and N-N bonds in these systems; however, no convergence of methyl signals could be observed with heating prior to the onset of decomposition.

Decomposition of Sulfoximines. Except for benzo derivative **14h,** these sulfoximines were photochemically quite stable when irradiated with a 450-W mercury lamp through Pyrex. The parent **14a** exhibits a broad absorption maximum at ca. 270 nm (ϵ 240) in its ultraviolet spectrum and, as expected, was responsive to more energetic radiation using a Vycor filter. Among the large number of products, a small amount (ca. 15%) of ethylene was identified (as ethylene dibromide).

Thermal decomposition of **14a,** on the other hand, was remarkably efficient (Scheme V). A solution of **14a** in diglyme, when heated to 110–130 °C, gave off a quantitative volume of ethylene, CO_2, and N_2 (determined gasimetrically), and left dimethyl sulfoxide as the sole compound in admixture with diglyme. The effluent gas from the reaction was swept in a stream of nitrogen through a trap containing bromine in methylene chloride, and the ethylene dibromide formed was identified both by infrared and gas chromatographic comparison with authentic material. The isolated yield of ethylene dibromide was 92%. Pyrolysis of **14b** and **14c** were likewise found to yield quantitative gas evolution and excellent yields of propylene, identified as 1,2-dibromopropane, and styrene, respectively. Sulfoximine **14d** was found to give *cis*-stilbene with no trace of the trans isomer, indicating that the extrusion reaction leading from diazene **4** to olefin is a stereospecific, syn elimination. Further support for this contention came from the observation that the mixture of sulfoximines **14f** and **14g** gave *trans*-2-pentene exclusively. Oxidation of *trans*-3-amino-4,5-diphenyl-2-oxazolidone (**7i**) with lead tetraacetate in Me_2SO led directly to *trans*-stilbene, the sulfoximine **14i** being too unstable for isolation. Olefin formation from the cyclooctyl compound **14e** was not completely stereospecific, affording a 82:18 mixture of *trans*:*cis*-cyclooctene. *trans*-Cyclooctene undergoes slow isomerization under the conditions of sulfoximine decomposition, and this may account for the loss of stereospecificity. Nevertheless, it was possible to isolate a 61% yield of *trans*-cyclooctene from this reaction. Decomposition of **14j** produced methylenecyclopentane without detectable contamination from endocyclic olefin, confirming the anticipated regiospecificity in this elimination (see Table II).

In contrast to the facile, thermal decomposition of these sulfoximines, the benzo analogue **14h** was quite stable up to 180 °C. Irradiation of **14h** with a sunlamp at 145–150 °C or with a Hanovia 450-W source through a Vycor filter in diglyme led to gas evolution but little CO_2 could be detected (with $Ba(OH)_2$), and the black, tarry residue could not be

Scheme VI

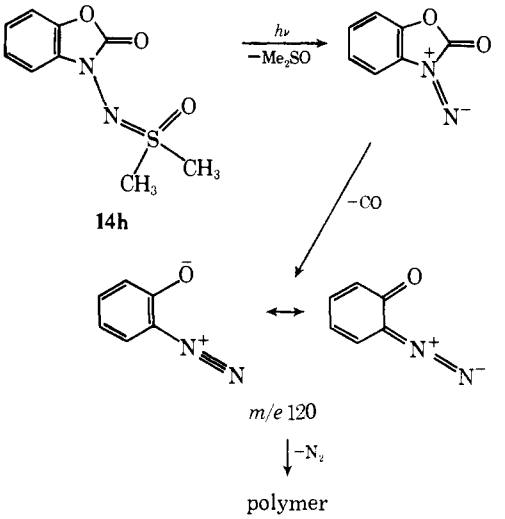


Table II. Decomposition of 3-Sulfoximino-2-oxazolidones

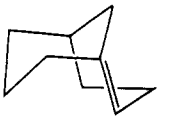
Sulfoximine	Olefin	Decomp. temp, °C	Yield, %
14a	Ethylene	110–130	92
14b	Propylene	110–130	91
14c	Styrene	120–140	94
14d	*cis*-Stilbene	120–140	97
14e	*trans*-Cyclooctene	110–120	61
14f, 14g	*trans*-2-Pentene	120–130	81
14h	Polymer	>180	
[**14i**]	*trans*-Stilbene	25–30	91
14j	Methylenecyclopentane	120	98

characterized. In agreement with results obtained by Rees,[13] benzyne was not a product of this reaction, as judged from our failure to intercept it as an adduct with tetraphenylcyclopentadienone. Interestingly, the mass spectrum of **14h** shows an intense, base peak at *m/e* 120.031, corresponding to a fragment $C_6H_4N_2O$, which implies an anomalous extrusion of carbon monoxide upon decomposition of this sulfoximine. Assuming a parallel sequence between mass spectrometric fragmentation and photochemical decomposition in the case of **14h,**[30] the pathway indicated in Scheme VI can be tentatively put forward.

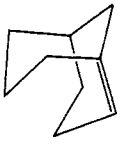
Bicyclo[3.3.1]non-1-ene. Application of the sulfoximine route to olefins described above to a synthesis of bicyclo[3.3.1]non-1-ene (**15**) appeared to offer a valid test of the

15

method for preparation of a strained and sensitive double bond.[31] Aside from its standing in formal violation of Bredt's rule,[32] **15** occupies a key position in the hierarchy of bridgehead olefins[33] in being the most strained, "anti-Bredt" hydrocarbon which has been isolated so far and whose properties have been studied in detail.[34] A further interesting feature of **15** is that two geometrically isomeric structures, **15a**(*Z*) and **15b**(*E*),



15a

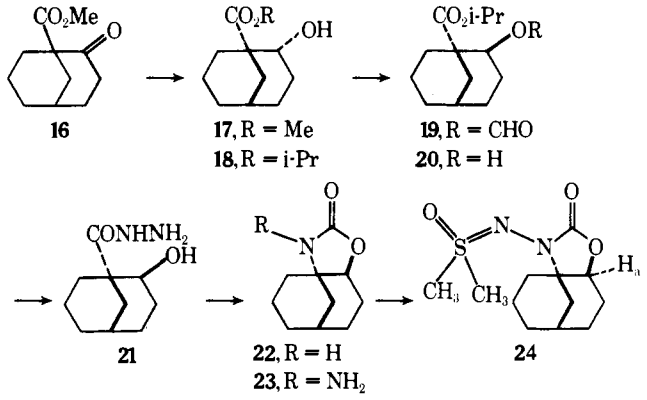


15b

can be distinguished in principle, with a (presumably) substantial energy barrier interposed between them.[35] Wiseman's postulate that the strain energy in a bridgehead alkene is closely related to the strain in the corresponding monocyclic *trans*-cycloalkene[36] leads to the prediction that **15a** (containing a *trans*-cyclooctene) will be appreciably more stable than **15b** (which would embody a *trans*-cyclohexene). The known stereospecificity in olefin formation from sulfoximines (see Scheme V) thus afforded an ideal opportunity not only for testing Wiseman's proposition, but also for probing the nature of **15b.** The existing methods[34,37] for synthesis of **15** do not permit a distinction to be made between *Z* and *E* isomers, and the low yields of this hydrocarbon obtained in earlier investigations may reflect this lack of discrimination.

For the preparation of the required, stereoisomeric sulfoximines, it was necessary to have access to exo and endo alcohols, **20** and **17.** Reduction of keto ester **16**[34] (Scheme VII) with sodium borohydride afforded an excellent yield of **17** and rather than try to exploit circumstances which might reverse this stereochemical preference, it was decided to effect inversion of the hydroxyl function at position 2. This was accomplished by a method analogous to that employed for configu-

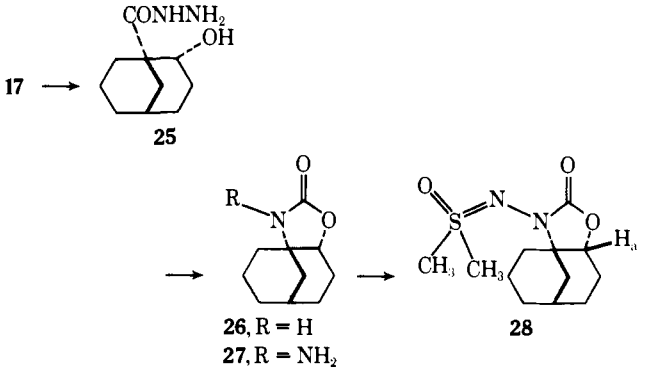
Scheme VII



rational inversion in the sterols,[38] and entailed conversion of endo alcohol **18** to its tosylate, followed by treatment with tetramethylammonium formate in dimethylformamide. The resulting exo formate **19** was saponified to the corresponding exo alcohol **20** without damage to the more hindered, bridgehead ester grouping. The overall yield for this inversion was 28%, but was nevertheless an improvement over the tedious gas chromatographic separation necessary to remove the major endo alcohol **18** from **20** in the mixture obtained by Meerwein-Ponndorf reduction of **16.** Treatment of **20** with hydrazine, followed by nitrosation of carbohydrazide **21,** furnished oxazolidone **22.** Amination of **22** with butyllithium and *O*-(2,4-dinitrophenyl)hydroxylamine gave *N*-aminooxazolidone **23,** which was promptly oxidized with lead tetraacetate in Me_2SO. The structure of the resulting, crystalline sulfoximine **24** was apparent from its infrared (1750 cm^{-1}) and NMR spectra, the latter exhibiting a triplet for the endo proton H_a at δ 4.26.

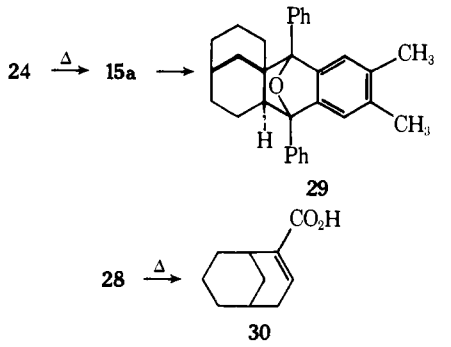
A parallel sequence (Scheme VIII), departing from endo

Scheme VIII



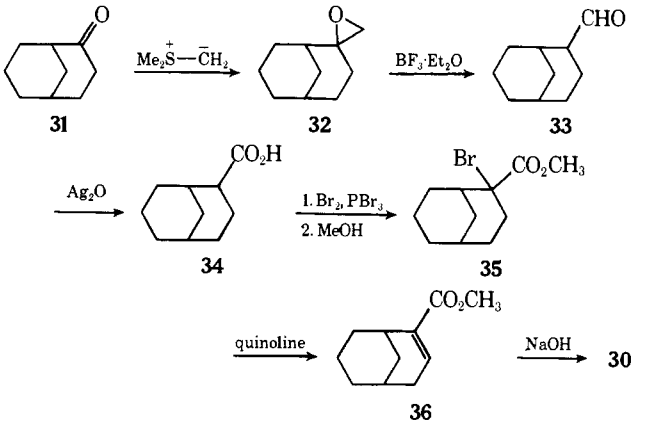
hydroxy ester **17,** proceeded via carbohydrazide **25** to endo oxazolidone **26.** Attempts to introduce the *N*-amino function in this case were confronted by an exceedingly reluctant substrate which failed to react with *O*-(2,4-dinitrophenyl)hydroxylamine. Fortunately, timely announcement of the powerful aminating agent, *O*-mesitylenesulfonylhydroxylamine,[39] enabled the preparation of **27** in 48% yield. Oxidation of **27** with lead tetraacetate in Me_2SO took place without incident to give crystalline sulfoximine **28,** in which the exo H_a proton appeared at δ 4.15.

Examination of the configurations of stereoisomeric sulfoximines **24** and **28** shows that a syn elimination should afford **15a** in the former case and **15b** from the latter. In fact, a solution of **24** in Me_2SO, when warmed to 120 °C, exhibited brisk gas evolution and an immediate, powerfully olefinic odor. Assay of the reaction mixture by NMR indicated the formation of bicyclo[3.3.1]non-1-ene in >80% yield; after washing to remove Me_2SO and distillation, a 53% yield of pure **15a** was obtained. The NMR spectrum of this material was identical with that published[34] and, in addition, **15a** gave a Diels-Alder adduct **29** with 1,3-diphenyl-5,6-dimethylisobenzofuran[40] which was fully characterized.



In contrast, heating **28** gave no trace of bicyclo[3.3.1]non-1-ene, but instead, at 150 °C, there was produced a crystalline compound, $C_{10}H_{14}O_2$, in 49% yield, with the properties of a carboxylic acid (2700 cm^{-1}, broad; δ 11.5, one proton, exchanged with D_2O). The infrared spectrum (1680, 1640 cm^{-1}) further indicated that this was an $\alpha\beta$-unsaturated acid, and a one-proton signal (triplet) at δ 7.08, as well as a readily discernible bridghead proton at δ 2.42 (also a triplet), was most easily accommodated by structure **30.** Proof of structure was provided by an independent synthesis of **30** shown in Scheme IX. Bicyclo[3.3.1]nonan-2-one (**31**)[41] was converted to the

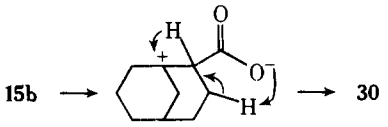
Scheme IX



spiro epoxide **32** with dimethylsulfonium methylide[42] and thence to aldehyde **33** upon treatment with boron trifluoride etherate. Oxidation of **33** afforded oily carboxylic acid **34** in 23% overall yield from **31.** α-Bromination of **34,** followed by esterification, gave **35** which underwent dehydrobromination with quinoline to yield $\alpha\beta$-unsaturated ester **36.** Finally, saponification of **36** gave an acid, identical by infrared and mass spectral comparison with the substance **30** obtained from the decomposition of **28.**[43]

The failure of **28,** in contrast to **24,** to produce any trace of bicyclo[3.3.1]non-1-ene is significant in light of the anticipated difference in strain energy between **15a** and **15b.** A force field calculation by Allinger and Sprague[44] places the strain energy associated with the bridgehead double bond of **15a** at 12.85 kcal/mol, in good agreement with the value (ca. 12 kcal/mol) determined calorimetrically from the acetolysis of **15a.**[45] *trans*-Cyclohexene is calculated to be 42.4 kcal/mol more strained than its cis counterpart, with ca. 31 kcal/mol of this strain residing in torsional energy across $C_{(1)}$-$C_{(2)}$.[44] Presumably all of this exaltation should appear in **15b,** and, after allowing for removal of residual strain (9 kcal) in the cyclooctene framework, *E* isomer **15b** is estimated to possess 45 kcal/mol of strain energy.

Several lines of evidence, both theoretical[44,46] and experimental,[47] suggest that severely twisted double bonds undergo rehybridization in the direction $sp^2 \rightarrow sp^3$. This process allows improved overlap of the realigned p orbitals and, hence, a measure of stabilization. The consequences of this rehybridization in terms of reactivity have not been specified, but one possible outcome is an increased polarization of the C=C bond.[48] Thus, trapping of **15b** with extruded CO_2 could lead to **37** and, following a 1,2-hydride shift toward the bridge-



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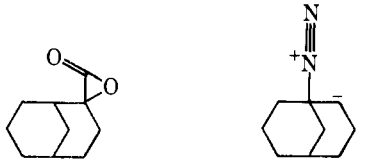
head,[49] proton elimination results in **30.** In justification of bridgehead cation **37,** it should be pointed out that a calculation by Gleicher and Schleyer estimates the strain energy of the bicyclo[3.3.1]non-1-yl carbonium ion at 14.8 kcal/mol,[50] so that the conversion **15b** → **37** would be appreciably exothermic.

Although mechanisms can be envisaged for the formation of **30** from **28** which circumvent **15b,** they require improbable intermediates. α-Lactone **38** can be dismissed on the basis of the known propensity of this very reactive functionality to undergo polymerization to a polyester at −100 °C;[51] other species (e.g., **39**) would be expected to afford relatively easy



38 39

access to **15a.** The energy barrier interposed between *E* olefin **15b** and the *Z* form **15a** is difficult to calculate, due to uncertainty regarding the precise pathway which this cis/trans isomerization must follow. A crude estimate of $\Delta H^{\ddagger}$ for the conversion of *trans*-cyclohexene to its cis isomer[44] places an upper limit of ca. 13 kcal/mol on this process. The bridged system of bicyclo[3.3.1]non-1-ene is likely to raise this barrier considerably higher, so that **15b** is compelled to find an alternate escape. Thus, the sulfoximine route to olefins affords not only an efficient route to bicyclo[3.3.1]non-1-ene (**15a**) but, on the basis of the tentative intermediacy of **15b,** may also provide access to systems with more highly strained carbon–carbon double bonds.

Experimental Section

Melting points were determined on a Kofler hot-stage microscope and are corrected; boiling points are uncorrected. Infrared (IR) spectra were recorded on a Perkin-Elmer 137 spectrophotometer. Nuclear magnetic resonance (NMR) spectra were measured on a Varian HA-100 spectrometer. Peak positions are given in parts per million (δ) downfield from tetramethylsilane as internal standard. The abbreviations s, d, t, q, and m refer to singlet, doublet, triplet, quartet, and multiplet, respectively; coupling constants are given in Hertz. Mass spectra, including accurate mass determinations, were obtained using a CEC-103B spectrometer; the abbreviation M^+ refers to the molecular ion. Thin-layer chromatograms (TLC) were made on Merck silica gel GF-254. Vapor phase chromatography (VPC) was carried out using a Varian Aerograph Model 700 instrument.

3-Amino-2-oxazolidone (7a). A. From 2-Hydroxyethylhydrazine. Following a published procedure,[18] a solution of sodium methoxide (from 0.60 g of sodium) in 60 ml of methanol was added to a solution of 15.2 g (0.01 mol) of 2-hydroxyethylhydrazine and 30.0 g (0.25 mol) of diethyl carbonate in 90 ml of methanol. The mixture was heated at reflux for 2 h, after which the solvent and unreacted diethyl carbonate were removed by vacuum distillation. The oily residue was diluted with hot ethanol and filtered, and the filtrate was allowed to cool to room temperature. The material deposited was recrystallized from ethanol to give 10.6 g (60%) of **7a**: mp 70–71 °C (lit.[18] 71 °C); IR (Nujol) 1750 and 3550 cm^{-1}; NMR ($CDCl_3$) δ 3.71 (3 H, t, J = 6 Hz), 4.14 (2 H, broad s, exchanged with D_2O), and 4.33 (3 H, t, J = 6 Hz).

B. Amination of 2-Oxazolidone. To a solution of 0.22 g (2.50 mmol) of 2-oxazolidone (Aldrich reagent) in 10 ml of dry THF cooled to −78 °C under a nitrogen atmosphere was added 1.4 ml of a 1.9 N solution of butyllithium in hexane by syringe through a rubber septum. The dark mixture was allowed to warm to −10 °C with stirring and then cooled to −50 °C before a solution of 0.52 g (2.61 mmol) of *O*-(2,4-dinitrophenyl)hydroxylamine in 10 ml of dry THF was added. The solution was allowed to warm to room temperature and then was heated at reflux for 5 h. The reaction mixture was diluted with 100 ml of dichloromethane and washed with 10% aqueous sodium carbonate and water and dried (Na_2SO_4). Evaporation of the solvent, followed by purification of the residue by preparative TLC (100% ethanol) gave, from a band at R_f 0.28, 0.095 g (38%) of **7a** identical with material prepared as described above.

3-Amino-5-methyl-2-oxazolidone (7b). A mixture of 2.0 g (0.022 mol) of 2-hydroxypropylhydrazine,[20] 2.62 g (0.023 mol) of diethyl carbonate, and 0.15 g of sodium in 13 ml of methanol was stirred under reflux for 0.5 h. The reaction vessel was then connected to a short-path still and ca. 15 ml of distillate was collected. To the residual, viscous oil was added (with ice cooling) a solution of 3 ml of concentrated hydrochloric acid in 20 ml of ethanol. This mixture, containing the aminooxazolidone hydrochloride, was evaporated to dryness and then taken up into 100 ml of ethanol. An excess (ca. 10 g) of triethylamine was added, and, after stirring for 1 h, the mixture was filtered to remove triethylamine hydrochloride. Ether was added to the filtrate until no further precipitate formed, the mixture was filtered again, and the filtrate was dried (Na_2SO_4). Evaporation of the solvent afforded 2.45 g of slightly impure **7b** as a viscous oil. Purification was effected by TLC (ethyl acetate–methanol, 10:2): NMR ($CDCl_3$) δ 1.44 (3 H, d, J = 6 Hz), 3.29 (1 H, m), 3.82 (1 H, m), 3.8 (2 H, broad, exchanged with D_2O), 4.65 (1 H, m). The crude material was satisfactory for conversion to sulfoximine **14b.**

3-Amino-5-phenyl-2-oxazolidone (7c). To a solution of 50 g (1.0 mol) of hydrazine hydrate in 20 ml of ethanol was added dropwise, with stirring, 12.0 g (0.10 mol) of styrene oxide. The exothermic reaction brought the mixture to reflux. After addition was complete, the solvent was evaporated and the residual, viscous oil was dried over phosphorus pentoxide to furnish 15.3 g (100%) of 2-hydroxy-2-phenylethylhydrazine: NMR ($CDCl_3$) δ 2.78 (2 H, m), 3.97 (4 H, s, exchanged with D_2O), 4.92 (1 H, m), and 6.31 (5 H, m). Attempted distillation of this compound led to decomposition.

A mixture of 4.60 g (0.03 mol) of crude 2-hydroxy-2-phenylethylhydrazine, 4.0 g (0.03 mol) of diethyl carbonate, and 0.30 g of sodium in 10 ml of methanol was heated at reflux for 0.3 h. Workup as described for **7b** gave 0.86 g (16%) of **7c** after crystallization from ethanol–ether: IR (Nujol) 1740, 3160, and 3340 cm^{-1}; NMR ($CDCl_3$) δ 3.64 (1 H, m), 4.09 (1 H, m), 5.51 (1 H, m), 3.9 (2 H, broad), and 7.44 (5 H, s).

***cis*-3-Amino-4,5-diphenyl-2-oxazolidone (7d).** A mixture of 3.20 g (0.016 mol) of *trans*-stilbene oxide,[52] 10.0 g (0.20 mol) of hydrazine hydrate, and 20 ml of ethanol was heated at reflux for 12 h. The solvent and unreacted hydrazine hydrate were removed by distillation. Upon addition of 10 ml of cold water, the residual, viscous oil crystallized and was collected and dried over phosphorus pentoxide. There was obtained 3.55 g (95%) of *erythro*-2-hydroxy-1,2-diphenylethylhydrazine as a colorless, unstable, crystalline solid: NMR (Me_2SO) δ 3.5 (2 H, broad, exchanged with D_2O), 3.83 (1 H, d, J = 5 Hz), 4.83 (1 H, d, J = 5 Hz), and 7.19 (10 H, s). Upon exposure to air this compound became yellow and amorphous; it was used for the next step without further purification.

A mixture of 3.55 g (0.015 mol) of *erythro*-2-hydroxy-1,2-diphenylethylhydrazine, 2.50 g (0.02 mol) of diethyl carbonate, and 0.20 g of sodium in 20 ml of methanol was heated at reflux for 0.5 h. Workup as described for **7b** yielded 1.27 g (31% based on stilbene oxide) of **7d** after crystallization from chloroform–hexane: IR (Nujol) 1750, 3240, and 3380 cm^{-1}; NMR ($CDCl_3$) δ 3.97 (2 H, s, exchanged with D_2O), 5.13 (1 H, d, J = 6 Hz), 5.84 (1 H, d, J = 6 Hz), 6.8–7.4 (10 H, m).

***trans*-3-Amino-4,5-hexamethylene-2-oxazolidone (7e). A. From Cyclooctene Oxide.** A mixture of 40.0 g (0.32 mol) of *cis*-cyclooctene

oxide[53] and 100 g (2.0 mol) of hydrazine hydrate in 100 ml of ethanol was placed in an autoclave and heated at 150 °C for 48 h. The reaction mixture was filtered, and the filtrate was evaporated in vacuo to leave a viscous oil. Addition of ether caused crystallization, and the solid was collected by filtration under nitrogen and dried over phosphorus pentoxide for 10 h. There was obtained 42.0 g (84%) of *trans*-2-hydroxycyclooctylhydrazine as a hygroscopic, straw-colored, crystalline solid, which became amorphous upon exposure to air: NMR ($CDCl_3$) δ 1.30–2.05 (12 H, m), 2.72 (1 H, m), 3.32–4.08 (5 H, broad, 4 H exchanged with D_2O).

A mixture of 3.20 g (0.02 mol) of *trans*-2-hydroxycyclooctylhydrazine, 2.50 g (0.02 mol) of diethyl carbonate, and 0.20 g of sodium in 20 ml of methanol was heated at reflux for 0.5 h. Workup as described for **7b** afforded 0.81 g (21%) of **10e** as an unstable oil. This material was converted promptly to its crystalline sulfoximine derivative (**14e**).

B. Amination of *trans*-4,5-Hexamethylene-2-oxazolidone (10b). To a solution of 0.40 g (2.4 mmol) of **10b** in 10 ml of dry THF at −78 °C was added dropwise 2.0 ml of a 1.5 N solution of *n*-butyllithium in hexane via a motor-driven syringe. The mixture was allowed to warm to 0 °C and held at this temperature for 10 min. The mixture was cooled again to −78 °C as a solution of 0.50 g (2.5 mmol) of *O*-(2,4-dinitrophenyl)hydroxylamine in 5 ml of dry THF was added by syringe. The dark-colored reaction mixture became red upon warming to room temperature, and, after stirring for 3 h, the mixture was heated at reflux for 0.5 h. Workup as described for **10a** (method B) gave 56 mg (12%) of **7e**, as a pale-yellow oil, identical with material prepared as described above: IR (neat) 1760 and 3400 cm^{-1}; NMR ($CDCl_3$) δ 1.0–2.6 (12 H), 3.43 (1 H, m), 3.88 (2 H, s, exchanged with D_2O), and 4.25 (1 H, m).

***trans*-3-Amino-4-ethyl-5-methyl-2-oxazolidone (7f) and *trans*-3-Amino-5-ethyl-4-methyl-2-oxazolidone (7g).** To a solution of 3.44 g (0.04 mol) of *cis*-2-pentene oxide[54] in 20 ml of ethanol at reflux was added dropwise, through a condenser, a solution of 15.0 g (0.3 mol) of hydrazine hydrate in 20 ml of ethanol. The mixture was heated at reflux for 10 h and was then distilled to give 3.30 g (70%) of a mixture of *threo*-2-hydrazino-3-hydroxypentane and *threo*-3-hydrazino-2-hydroxypentane; bp 86–90 °C (0.5 mm).

A solution of 1.18 g (0.01 mol) of the mixture of hydrazinohydroxypentanes and 1.50 g (0.01 mol) of diethyl carbonate in 10 ml of methanol was added to a solution of 0.10 g of sodium in 10 ml of methanol. The mixture was heated at reflux for 0.5 h and workup as described for **7b**, afforded 0.66 g (46%) of a mixture of **7f** and **7g**. This mixture could be separated by preparative TLC (1:1 ether–cyclohexane) and gave a pure isomer: IR (neat) 1750 and 3400 cm^{-1}; NMR ($CDCl_3$) δ 1.1 (6 H, m), 1.74 (2 H, m), 3.7 (2 H, m), and 4.08 (2 H, s, exchanged with D_2O). The second isomer was impure.

***trans*-4,5-Hexamethylene-2-oxazolidone (10b).** A solution of 0.70 g (4.9 mmol) of *trans*-2-aminocyclooctanol (**9b**)[22] in 100 ml of dry THF was added dropwise during 2 h to a stirred solution of *N,N'*-carbonyldiimidazole [prepared from 1.70 g (25 mmol) of imidazole according to the method of Staab[55]] in 50 ml of dry THF. After addition was complete, the reaction mixture was stirred at room temperature for 3 h and then heated at reflux for 1 h. The mixture was diluted with 150 ml of ether and washed five times with 1 N sulfuric acid and once with brine. The organic extract was dried (Na_2SO_4), and the solvent was evaporated to leave a viscous oil. Preparative TLC (1:1 ether–cyclohexane) afforded 0.43 g (52%) of **10b** as an oil; IR (neat) 1770 and 3350 cm^{-1}; NMR ($CDCl_3$) δ 0.8–2.5 (12 H), 3.75 (1 H, m), 4.45 (1 H, m), and 6.8 (1 H, broad, exchanged with D_2O); *m/e* 169 (M^+).

***trans*-3-Amino-4,5-diphenyl-2-oxazolidone (7i).** A solution of 120 mg (0.50 mmol) of *trans*-4,5-diphenyl-2-oxazolidone (**10a**)[24] in 10 ml of dry THF was cooled to −60 °C and 0.45 ml of a 1.5 N solution of *n*-butyllithium in hexane was added with stirring. After 10 min, the mixture was allowed to warm to −20 °C and held at this temperature for 3 min. The mixture was cooled again to −60 °C as a solution of 100 mg (0.50 mmol) of *O*-(2,4-dinitrophenyl)hydroxylamine in 5 ml of dry THF was added by syringe through a septum. The mixture was allowed to warm to room temperature, stirred for 5 h, and then heated at reflux for 0.5 h. Workup as described for **7a** (method B) furnished a solid which was crystallized from hexane to give 35 mg (28%) of **7i**; IR (Nujol) 1770 and 3420 cm^{-1}; NMR ($CDCl_3$) δ 3.93 (2 H, s, exchanged with D_2O), 4.55 (1 H, d, J = 6 Hz), 5.20 (1 H, d, J = 6 Hz), and 7.36 (10 H, m). Anal. ($C_{15}H_{14}N_2O_2$) C, 70.74; H, 5.58; N, 10.39.

3-Amino-4,5-benzooxazolin-2-one (7h). A solution of 1.35 g (0.01 mol) of 4,5-benzooxazolin-2-one[56] in 20 ml of dry THF was cooled to −78 °C and 4.4 ml of a 2.4 N solution of *n*-butyllithium in hexane was added with stirring. This mixture was allowed to react, as described for **7i**, with 2.00 g (0.01 mol) of *O*-(2,4-dinitrophenyl)hydroxylamine. After the reaction was complete (1 h at reflux), the mixture was diluted with 150 ml of dichloromethane, and the solution was washed with water and dried (Na_2SO_4). Evaporation of the solvent left a solid which was crystallized from ethanol to give 1.22 g (81%) of **7h** as colorless rods, mp 169–170 °C (lit.[13] 168–171 °C).

1-Hydroxycyclopentylacetohydrazide (12). A mixture of 8.50 g (0.052 mol) of ethyl 1-hydroxycyclopentylacetate (**11**)[26] and 15.0 g (0.30 mol) of hydrazine hydrate was allowed to stand at room temperature for 10 h. After the unreacted hydrazine hydrate had been removed in vacuo, the solid residue was collected and was crystallized from ethanol to give 6.90 g (86%) of **12**: mp 144–146 °C; IR (Nujol) 1690, 3370, and 3600 cm^{-1}; NMR (Me_2SO-d_6) δ 1.55 (8 H, s), 2.25 (2 H, s), 4.23 (2 H, S, exchanged with D_2O), 4.63 (1 H, s, exchanged with D_2O), and 8.97 (1 H, s, exchanged with D_2O).

Spiro[5,5-tetramethylene-2-oxazolidone] (13). A solution of 6.50 g (0.041 mol) of **12** in 30 ml of 6 N hydrochloric acid was cooled to −5 °C, and a solution of 3.00 g (0.045 mol) of sodium nitrite in 30 ml of water was added. The mixture was stirred at −5 °C for 1 h and extracted with 500 ml of a 3:1 benzene–chloroform mixture. This extract was washed with saturated sodium chloride solution, dried (Na_2SO_4), and added dropwise to a small quantity (ca. 20 ml) of benzene at reflux. Reflux was maintained throughout addition, after which the solvent was evaporated. The residue was purified by precipitation from chloroform solution with hexane, followed by sublimation at 90–100 °C (0.10 mm), and afforded 5.30 g (79%) of **13**: mp 97–99 °C; IR (Nujol) 1760 and 3300 cm^{-1}; NMR ($CDCl_3$) δ 1.5–2.3 (8 H, m), 3.53 (2 H, s), and 6.61 (1 H, broad); *m/e* 141 (M^+).

Nitrosation of **13** (1.41 g, 0.01 mol) in 6 N hydrochloric acid by addition of this solution in small portions to 0.75 g (0.01 mol) of sodium nitrite in water yielded 1.65 g (96%) of *N*-nitroso derivative: mp 97–98 °C; IR (Nujol) 1780 cm^{-1}; *m/e* 170 (M^+).

Spiro[3-amino-5,5-tetramethylene-2-oxazolidone] (7j). A solution of 0.35 g (2.5 mmol) of **13** in 30 ml of dry THF was cooled to −78 °C and 1.35 ml of a 1.9 N solution of *n*-butyllithium in hexane was added. Amination with 0.50 g (2.5 mol) of *O*-(2,4-dinitrophenyl)hydroxylamine in 5 ml of dry THF, followed by workup, as described for **7a** (method B) gave an oil, which was purified by preparative TLC (ether). Eluted material was crystallized from hexane to give 0.15 g (39%) of **7j**: IR (Nujol) 1745, 3250 and 3400 cm^{-1}; NMR ($CDCl_3$) δ 1.5–2.3 (8 H, m), 3.60 (2 H, s), and 3.9 (2 H, broad, exchanged with D_2O); *m/e* 156 (M^+).

Preparation of 3-Dimethylsulfoximino-2-oxazolidones (14a–j). A general procedure was followed in which lead tetraacetate (0.01 mol) was added in small portions to the 3-amino-2-oxazolidone (**7a–j**, 0.01 mol) in 20 ml of a stirred, 1:4 mixture of dichloromethane–dimethyl sulfoxide at 0 °C. The reaction mixture was stirred for 2 h in an ice bath and was allowed to warm to room temperature. The mixture was diluted with 200 ml of dichloromethane and washed with 3 × 30 ml of saturated sodium chloride solution. The organic layer was dried (Na_2SO_4), and the solvent was evaporated. The residue was crystallized (except **14f**, **14g**, and **14i**) from ether–dichloromethane:

14a: IR (Nujol) 1750 cm^{-1}; NMR ($CDCl_3$) δ 3.20 (6 H, s), 3.75 (2 H, t, J = 6 Hz), and 4.40 (2 H, t, J = 6 Hz); *m/e* 178 (M^+). Anal. ($C_5H_{10}N_2O_3S$) C, 33.71; H, 5.65; N, 15.63.

14b: IR (Nujol) 1760 cm^{-1}; NMR ($CDCl_3$) δ 1.45 (3 H, d, J = 6 Hz), 3.19 (3 H, s), 3.21 (3 H, s), 3.35 (1 H, t, J = 7 Hz), 3.83 (1 H, t, J = 7 Hz), and 4.7 (1 H, m); *m/e* 192 (M^+). Anal. ($C_6H_{12}N_2O_3S$) C, 37.16; H, 6.28; N, 14.78.

14c: IR (Nujol) 1760 cm^{-1}; NMR ($CDCl_3$) δ 3.17 (3 H, s), 3.20 (3 H, s), 3.67 (1 H, t, J = 7 Hz), 4.08 (1 H, t, J = 7 Hz), 5.54 (1 H, t, J = 7 Hz), and 7.42 (5 H, s); *m/e* 254 (M^+). Anal. ($C_{11}H_{14}N_2O_3S$) C, 52.05; H, 5.52; N: calcd, 11.02; found, 11.58.

14d: IR (Nujol) 1755 cm^{-1}; NMR (Me_2SO-d_6) δ 3.17 (3 H, s), 3.22 (3 H, s), 5.21 (1 H, d, J = 7 Hz), 6.06 (1 H, d, J = 7 Hz), and 6.75–8.25 (10 H, m). Anal. ($C_{17}H_{18}N_2O_3S$) C, 61.37; H, 5.49; N, 8.20.

14e: IR (Nujol) 1750 cm^{-1}; NMR ($CDCl_3$) δ 1.10–1.56 (12 H), 3.15 (3 H, s), 3.19 (3 H, s), 3.50 (1 H, m), and 4.40 (1 H, m); *m/e* 260 (M^+). Anal. ($C_{11}H_{20}N_2O_3S$) C: calcd, 50.74; found, 51.16; H, 7.93; N, 10.57.

14f and **14g** were prepared as a ca. 1:1 mixture from a mixture of

7f and **7g**: IR (neat) 1750 cm^{-1}; NMR ($CDCl_3$) δ 0.78–1.85 (8 H), 3.18 (3 H, s), 3.22 (3 H, s), 3.40 (1 H, m), and 3.80–4.40 (1 H); *m/e* 220 (M^+).

14h: IR (Nujol) 1760 cm^{-1}; NMR (Me_2SO-d_6) δ 3.38 (6 H, s) and 7.17 (4 H, m); *m/e* 226 (M^+). Anal. ($C_9H_{10}N_2O_3S$) C, 48.06; H, 4.51; N, 12.50.

14j: IR (Nujol) 1750 cm^{-1}; NMR ($CDCl_3$) δ 1.48–2.26 (8 H) 3.18 (6 H, s), and 3.66 (2 H, s); *m/e* 232 (M^+). Anal. ($C_9H_{16}N_2O_3S$) C, 46.35; H, 6.98; N, 12.24.

Thermal Decomposition of 3-Dimethylsulfoximino-2-oxazolidones. A solution of 0.6–4 mmol of the sulfoximine in 5–20 ml of Me_2SO was heated to 140 °C for 2 h. Vigorous gas evolution began ca. 90 °C (except with **14h**). Ethylene and propylene, from **14a** and **14b**, respectively, were swept through a solution of bromine (10–20 mmol) in 200 ml of dichloromethane. The solution was washed with a 20% aqueous solution of sodium bisulfite, followed by a saturated solution of sodium bicarbonate and water. The organic layer was dried (Na_2SO_4) and the solvent was distilled to leave a residual oil, shown by NMR to be virtually pure 1,2-dibromoalkane. This material was subjected to VPC on a 5 ft × 0.25 in, 15% SE-30 column at 100 °C, and the pure dibromide was collected and identified by comparison (IR) with an authentic sample.

The volatile products from decomposition of the mixture of **14f** and **14g** were swept into a trap maintained at −100 °C. The deposited oil was taken up into carbon tetrachloride, and the solution was dried (Na_2SO_4). Distillation yielded pure *trans*-2-pentene, bp 38 °C, identical with an authentic sample.

The reaction mixture from **14j** was distilled without processing (bath temperature 120 °C), and the distillate was shown to be pure methylenecyclopentane by comparison with an authentic sample.

In the case of **14c** and **14d** the decomposition was run in Me_2SO-d_6 as solvent, and the reaction mixture was analyzed by NMR following completion of the reaction. The product from **14c** was shown to be styrene by comparison of the NMR spectrum with that of an authentic sample; ca. 6% of polystyrene was present which was removed by centrifugation. The product from **14d** was shown to be *cis*-stilbene by comparison of its NMR and UV spectra with those of an authentic sample. Yield data for styrene and *cis*-stilbene are based upon NMR determination using standard solutions.

The reaction mixture from **14e** showed a ratio of trans/cis cyclooctene of 82:18, as determined from the integrated vinyl proton signals in the NMR spectrum. The mixture was subjected to VPC on a 6 ft × 0.25 in., 16% Carbowax 20 M column at 70 °C to give *trans*-cyclooctene (R_t 4.2 min), whose IR and NMR spectrum were identical with those of an authentic sample,[57] followed by *cis*-cyclooctene (R_t 5.6 min).

***trans*-Stilbene.** A stirred solution of 25 mg (0.10 mmol) of **7i** in 2 ml of dichloromethane–Me_2SO (1:1) was cooled to 0 °C and 44 mg (0.10 mmol) of lead tetraacetate was added. The mixture was stirred for 2 h at 0 °C and then allowed to warm to room temperature. Workup as described for **14a–j** afforded a solid which was crystallized from hexane to give 16.0 mg (91%) of *trans*-stilbene: mp 123–124 °C (lit.[58] 123–124 °C).

Irradiation of 3-Dimethylsulfoximino-2-oxazolidone (14a). A solution of 1.00 g (5.6 mmol) of **14a** in 100 ml of water was irradiated with a Hanovia 450-W, medium-pressure, mercury lamp through a Vycor filter for 3 h while a stream of nitrogen was passed through the solution. The effluent gas was passed through a trap containing ca. 3 g of bromine in 200 ml of dichloromethane. The dichloromethane solution was washed with a saturated, aqueous solution of sodium sulfite until it was colorless, and was dried (Na_2SO_4). The solvent was removed by distillation, and the residue was subjected to VPC on a 5 ft × 0.25 in., 15% SE-30 column at 100 °C. Five compounds were eluted in the ratio 6:6:5:10:20. The material corresponding to the second peak in order of elution was collected and identified from its IR and NMR spectra (δ 3.55, singlet) as 1,2-dibromoethane. The yield of ethylene, based upon a quantitative estimation by VPC of the dibromide, was 15%.

Isopropyl *exo*-2-Hydroxybicyclo[3.3.1]nonan-1-carboxylate (20). A solution of 1.20 g (5.3 mmol) of **18**[34] in 15 ml of pyridine was cooled to 0 °C and 3.0 g (15.0 mmol) of *p*-toluenesulfonyl chloride was added. The mixture was stirred at 0 °C for 6.5 h and poured into ice–water. The solid which separated was collected by filtration and dried in vacuo to give 2.0 g (99%) of virtually pure tosylate: mp 92–95 °C; NMR ($CDCl_3$) δ 1.18 (6 H, d, J = 6 Hz), 1.3–2.3 (13 H), 2.40 (3 H, s), 4.80 (1 H, m), 5.25 (1 H, t, J = 6 Hz), and 7.50 (4 H, m).

A mixture of 2.0 g (5.3 mmol) of tosylate and 4.0 g (23 mmol) of tetraethylammonium formate in 50 ml of dimethylformamide was stirred at 80 °C for 83 h. The mixture was diluted with 100 ml of ether, washed with water, and dried (Na_2SO_4). After the solvent had been evaporated, a suspension of 2.0 g (24 mmol) of sodium bicarbonate in 30 ml of methanol was added, and the mixture was stirred for 6 h. The mixture was diluted with 200 ml of ether, washed with water, and dried (Na_2SO_4). The volume of solvent was reduced to a few milliliters, and the concentrate was chromatographed on silica gel. Elution with hexane–ether (1:1) gave ca. 0.5 g of a substance identified as isopropyl bicyclo[3.3.1]non-2-en-1-carboxylate, followed by 305 mg (25%) of **20** as an oil. The IR and NMR spectra of **20** were identical with those of material obtained as the minor component in the mixture resulting from the Meerwein-Ponndorf reduction of **16**.[34]

***exo*-2-Hydroxybicyclo[3.3.1]nonan-1-carbohydrazide (21).** A mixture of 305 mg (1.35 mmol) of **20** and 1.0 g (20 mmol) of hydrazine hydrate in 5 ml of dioxane was sealed in a thick-walled tube and heated at 150–160 °C for 110 h. The reaction mixture was diluted with 100 ml of chloroform, washed with water, and dried (Na_2SO_4). The solvent was evaporated, and the solid residue was crystallized from pentane–ether to yield 0.205 g (76%) of **21**: mp 155–159 °C.

***exo*-Oxazolidone 22.** A solution of 54 mg (0.27 mmol) of **21** in 3 ml of 6 N hydrochloric acid was cooled to −5 °C and treated with 50 mg (0.59 mmol) of sodium nitrite. The mixture was stirred at −5 °C for 1 h and taken up into 200 ml of ice-cold benzene–chloroform (3:1). The organic layer was separated, washed twice with 10 ml of saturated sodium chloride solution, and dried (Na_2SO_4). This solution was added dropwise to benzene at reflux, and the mixture was heated at reflux for 0.5 h after addition was complete. The solvent was evaporated and the residue was taken up into ether, to which was added pentane until the solution became cloudy. After standing for 10 h at −10 °C, 44.6 mg (92%) of **22** was collected as colorless crystals: mp 121–123 °C; IR ($CHCl_3$) 1760 and 3350 cm^{-1}; NMR ($CDCl_3$) δ 0.9–2.5 (13 H), 4.33 (1 H, d of d, J = 9, 4 Hz), and 6.40 (1 H, broad, exchanged with D_2O); *m/e* 181 (M^+).

***exo*-Sulfoximine 24.** A solution of 130 mg (0.72 mmol) of **22** in 10 ml of dry THF at −78 °C was treated with 0.5 ml of a 2 N solution of *n*-butyllithium in hexane followed by 250 mg (1.25 mmol) of *O*-(2,4-dinitrophenyl)hydroxylamine in 10 ml of dry THF as described for **7a** (method B). Workup as previously described afforded an oil which, according to its NMR spectrum, consisted of a 1:1 mixture of **22** and **23**. This mixture was dissolved in 10 ml of Me_2SO–dichloromethane (4:1) at 0 °C and 300 mg (0.68 mmol) of lead tetraacetate was added. Workup as described for **14a–j** furnished a semisolid, which was chromatographed on silica gel. Elution with ether and then with ether containing 5% of methanol gave 60 mg of recovered **22** followed by 46 mg (45% based on **22**) of **24**: mp 109–110 °C dec; IR ($CHCl_3$) 1750 cm^{-1}; NMR ($CDCl_3$) δ 1.05–2.45 (13 H), 3.17 (6 H), and 4.26 (1 H, t, J = 6 Hz); *m/e* 272.122 (M^+, calcd for $C_{12}H_{20}N_2O_3S$, 272.119).

***endo*-2-Hydroxybicyclo[3.3.1]nonan-1-carbohydrazide (25).** A mixture of 1.38 g (7.0 mmol) of **17**[34] and 1.50 g (30 mmol) of hydrazine hydrate in 20 ml of ethanol containing 0.5 ml of water was sealed in a thick-walled, glass tube and heated at 150 °C for 12 h. The reaction mixture was diluted with 200 ml of a 1:1 mixture of chloroform–ether, washed with water, and dried (Na_2SO_4). Evaporation of the solvent left an oil which crystallized from hexane to give 0.31 g (40%) of **25**: mp 100–102 °C; IR (Nujol) 1670 and 3380 cm^{-1}; NMR (9:1 $CDCl_3$/acetone-d_6) δ 1.2–2.4 (13 H), 3.4–4.2 (4 H, broad m), and 10.6 (1 H, broad s).

***endo*-Oxazolidone 26.** A solution of 390 mg (1.97 mmol) of **25** in 6 N hydrochloric acid was nitrosated, and the resulting acyl azide was treated as described for **22** (ca. sevenfold scale). Following crystallization of the crude product from ether–pentane, there was obtained 230 mg (64%) of **26**: mp 87–89.5 °C; IR (Nujol) 1760 and 3450 cm^{-1}; NMR ($CDCl_3$) δ 1.15–2.40 (13 H), 4.18 (1 H, t, J = 8 Hz), and 5.90 (1 H, broad s, exchanged with D_2O).

***endo*-Sulfoximine 28.** A solution of 123 mg (0.68 mmol) of **26** in 20 ml of dry THF was cooled to −78 °C and 0.35 ml of a 2.3 M solution (0.77 mmol) of *n*-butyllithium was added. This mixture was stirred for 0.5 h and 350 mg (1.70 mmol) of *O*-mesitylenesulfonylhydroxylamine[59] was added. The mixture was allowed to warm to room temperature, stirred for 5 h, and heated at reflux for 0.5 h. The reaction mixture was diluted with 100 ml of ether, washed with water, and dried (Na_2SO_4). Evaporation of the solvent gave 108 mg of **27**

(ca. 80% pure), which was used without further purification.

A solution of 108 mg of crude **27** in 10 ml of Me_2SO–dichloromethane (4:1) was treated at 0 °C with 250 mg (0.56 mmol) of lead tetraacetate. Workup as described for **14a–j** gave an oil which was chromatographed on silica gel. Elution with ether, followed by ether containing 20% of methanol, gave 34 mg of **26** in the first fractions and subsequently 45 mg (34% based on **26**) of **28**: mp 131–133 °C dec; IR ($CHCl_3$) 1755 cm^{-1}; NMR ($CDCl_3$) δ 1.45–2.45 (13 H), 3.19 (3 H, s), 3.21 (3 H, s), and 4.15 (1 H, t, J = 6 Hz); *m/e* 272.118 (M^+, calcd for $C_{12}H_{20}N_2O_3S$, 272.119).

Bicyclo[3.3.1]non-1-ene (15). A solution of 22 mg (0.08 mmol) of **24** in 0.4 ml of Me_2SO-d_6 was heated at 125–130 °C for 0.5 h. Gas evolution was observed and a pungent odor was detected. The NMR spectrum of the reaction mixture contained a peak at δ 5.72 and other features which corresponded closely to the published[37] spectrum of **15**. The mixture was diluted with 100 ml of a 1:1 mixture of pentane–ether, washed with water, and dried (Na_2SO_4). Distillation through a short column of glass helices gave 5.2 mg (53%) of **23**, whose NMR spectrum was identical with that reported.[37]

A mixture of 5.2 mg (0.04 mmol) of **15** and 20 mg (0.07 mmol) of 5,6-dimethyl-1,3-diphenylisobenzofuran[40] in 15 ml of ether was allowed to stand at room temperature for 10 h. After evaporation of the solvent, the residue was chromatographed on silica gel. Elution with hexane–ether gave 9.6 mg (53%) of **29**: mp 212–214 °C; NMR ($CDCl_3$) δ 0.8–2.5 (14 H), 2.20 (6 H, s), and 6.8–7.8 (12 H); *m/e* 420.240 (M^+, calcd for $C_{31}H_{32}O$ 420.245). Anal. ($C_{31}H_{32}O$) C, 88.21; H, 7.54.

Bicyclo[3.3.1]nonan-1-carboxaldehyde (33). A mixture of 20 ml of Me_2SO (dried by distillation over calcium hydride) and 0.53 g (12 mmol) of a 50% suspension of sodium hydride in mineral oil, which had been washed three times with dry hexane, was heated at 70–75 °C until gas evolution ceased (ca. 1 h). To the stirred mixture at −5 °C was added 2.20 g (12 mmol) of trimethylsulfonium iodide in 20 ml of dry THF followed, after 5 min, by 1.38 g (10 mmol) of bicyclo[3.3.1]nonan-2-one.[41] The mixture was allowed to warm to room temperature and was stirred for 1 h. Dilution of the mixture with 150 ml of ether, followed by washing with water, drying (Na_2SO_4), and evaporation of the solvent, left crude **32** as an oil: NMR (CCl_4) δ 2.50 (2 H). This material was used in the following reaction without purification.

The crude epoxide, **32**, obtained above was dissolved in 30 ml of anhydrous ether containing 0.5 ml of boron trifluoride etherate. The mixture was stirred at 0 °C for 0.25 h and then washed with water and dried (Na_2SO_4). Evaporation of the solvent, followed by a rapid distillation at 0.1 mm (bath temperature 160 °C) gave 520 mg (34% based on **31**) of **33**: IR (neat) 1720 cm^{-1}; NMR (CCl_4) δ 1.0–2.7 (15 H) and 9.62 (1 H, d, J = 3 Hz); *m/e* 152 (M^+).

Bicyclo[3.3.1]nonan-2-carboxylic Acid (34). A mixture of 520 mg (3.4 mmol) of **33**, 2.34 g (10 mmol) of silver oxide, and 1.80 g (40 mmol) of sodium hydroxide in 30 ml of water was stirred at room temperature for 10 h. The mixture was filtered by suction, and the collected solids were washed with 3 × 30 ml portions of hot water. The combined filtrate was washed with ether and acidified at 0 °C to Congo red with concentrated hydrochloric acid. The mixture was extracted with 3 × 50 ml portions of ether, and the combined ether extract was washed with water and dried (Na_2SO_4). Evaporation of the solvent left 370 mg (65%) of virtually pure **34** as an oil: IR (neat) 1710 and 2800 cm^{-1}; NMR ($CDCl_3$) δ 1.0–2.9 (15 H) and 11.68 (1 H, broad s, exchanged with D_2O); *m/e* 168 (M^+).

Methyl Bicyclo[3.3.1]non-2-en-2-carboxylate (36).[60] To a stirred mixture of 320 mg (1.90 mmol) of **34** and 525 mg (1.94 mmol) of phosphorus tribromide in 10 ml of carbon tetrachloride was added dropwise 670 mg (4.0 mmol) of bromine. The mixture was heated at 85–90 °C for 18 h and then cooled in ice as 5 ml of methanol was slowly added. The resulting, orange-colored mixture was heated at reflux for 0.25 h and then diluted with 10 ml of saturated sodium sulfite solution. The mixture was extracted with ether, and the ethereal extract was washed with water and dried (Na_2SO_4). Evaporation of the solvent gave **35** as an oil: NMR (CCl_4) δ 3.8 (3 H, s).

The crude α-bromo ester (**35**) was dissolved in 15 ml of quinoline, and the solution was heated at 160–170 °C for 3 h. The dark mixture was diluted with 30 ml of 20% hydrochloric acid and extracted with ether. The ethereal extract was washed with 10% hydrochloric acid and water and dried (Na_2SO_4). Evaporation of the solvent, followed by rapid distillation at 0.1 mm (bath temperature 180 °C) gave 270 mg (81%) of **36**: IR (neat) 1725 cm^{-1}; NMR (CCl_4) δ 1.1–2.7 (12 H), 3.67 (3 H, s), and 7.05 (1 H, t, J = 5 Hz).

Bicyclo[3.3.1]non-2-en-2-carboxylic Acid (30). A. Thermal Decomposition of 28. A solution of 20 mg (0.07 mmol) of **28** in 0.3 ml of Me_2SO was heated at 150–160 °C for 1 h. The mixture was diluted with ether and washed with water. The organic layer was dried (Na_2SO_4), and the solvent was evaporated to leave a residue, which showed, aside from material at the origin, a single spot on TLC (ether, R_f 0.42). The residue was chromatographed on silica gel and eluted with ether to give 9.0 mg (49%) of **30**: mp 73–77 °C; IR (CCl_4) 1640, 1670, and 2700 (broad) cm^{-1}; NMR (CCl_4) δ 1.3–2.65 (11 H), 2.42 (1 H, t, J = 6 Hz), 7.08 (1 H, t, J = 6 Hz), and 11.5 (1 H, broad s, exchanged with D_2O); *m/e* 166.100 (M^+, calcd for $C_{10}H_{14}O_2$, 166.099).

B. Saponification of 36. A mixture of 270 mg (1.50 mmol) of **36** and 500 mg of potassium hydroxide in 10 ml of 50% aqueous ethanol was heated at reflux for 1.5 h. Ethanol was removed by distillation, and the reaction mixture was diluted with 50 ml of water and washed with 30 ml of ether. The aqueous phase was acidified to Congo red with concentrated hydrochloric acid and extracted with 150 ml of ether. The ethereal extract was washed with water and dried (Na_2SO_4). Evaporation of the solvent left an oil which was distilled (100–110 °C at 0.2 mm) to give 220 mg (89%) of **30**, identical by infrared and mass spectral comparison with material prepared by method A above.

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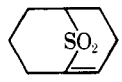

i

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Selective Trapping of Dienes by Benzylideneacetoneiron Tricarbonyl. Synthetic and Mechanistic Studies of the Reactions of 1,3,5-Cyclooctatriene and its Derivatives with Benzylideneacetoneiron Tricarbonyl

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Abstract: Thermal reactions of benzylideneacetoneiron tricarbonyl ($BDAFe(CO)_3$) with cyclooctatriene (**1**), bicyclo[6.2.0]decatriene (**5b**), bicyclo[6.1.0]nonatriene (**5a**), and *syn*-9-methylbicyclo[6.1.0]nonatriene (**17**) are reported. For **1**, **5b**, and **17**, $BDAFe(CO)_3$ selectively traps the diene tautomers present in low concentrations in equilibrium with the trienes to yield bicyclo[4.2.0]octadieneiron tricarbonyl (**4**), tricyclo[4.4.0.$0^{2,5}$]deca-7,9-dieneiron tricarbonyl (**7**), and *syn*-8-methyltricyclo[4.3.0.$0^{7,9}$]nona-2,4-dieneiron tricarbonyl (**19**), respectively, as the sole products of reaction in good yields. In the case of **5a**, the major product of reaction is tricyclo[4.3.0.$0^{7,9}$]nona-2,4-dieneiron tricarbonyl (**10**) (48%) but also found are *cis*-8,9-dihydroindeneiron tricarbonyl (**14**) (21%) and *cis*^{4}-cyclononatetraeneiron tricarbonyl (**15**) (9%) from trapping by $BDAFe(CO)_3$ of thermal rearrangement products of **5a**. Low temperature oxidative cleavage of **7**, **10**, and **19** with ceric ion yields the corresponding free diene ligands, tricyclo[4.4.0.$0^{2,5}$]deca-7,9-diene (**6b**), tricyclo[4.3.0.$0^{7,9}$]nona-2,4-diene (**6a**), and *syn*-8-methyltricyclo[4.3.0.$0^{7,9}$]nona-2,4-diene (**18**). Rates for the electrocyclic ring openings of the dienes to the trienes have been measured for **6b**, **6a**, and **18** and the equilibrium ratio of triene:diene tautomers has been determined to be 40 for **5b**:**6b** and estimated as 4500 for **5a**:**6a** and **17**:**18**. A kinetic study of the reaction of excess $BDAFe(CO)_3$ with **1** has revealed that the rate-limiting step is the ring closure of the triene **1** to the diene **2** and the selectivity of $BDAFe(CO)_3$ results from a kinetic selectivity for the diene relative to the triene. A study of the kinetics of the reaction of $BDAFe(CO)_3$ with 1,3-cyclohexadiene to yield cyclohexadieneiron tricarbonyl suggests a mechanism which involves dechelation of the carbonyl group of the bound enone to form a four-coordinate, 16 electron iron complex which is then trapped by cyclohexadiene.

The manner in which the stabilities and reactivities of polyolefins are modified by coordination to transition metals has received considerable attention over the past several years. One of the most interesting and synthetically useful applications in this area has been the preparation of transition metal complexes of highly reactive polyolefins which are not normally stable at ambient temperatures. For example, the iron tricarbonyl moiety has been extensively used to stabilize as iron