Reaction of Chlorosulfonyl Isocyanate with Triene Systems[1a,b]

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Received April 8, 1976

A number of trienes were treated with chlorosulfonyl isocyanate (CSI). In general, the reaction of CSI with cyclic trienes gave only 1,6-cycloaddition products. The 7-substituted cycloheptatrienes gave *N*-chlorosulfonylimino ethers while the 1- and 3-substituted cycloheptatrienes gave *N*-chlorosulfonyllactams. The reaction of CSI with the unconjugated triene 1,5,9-cyclododecatriene gave only an unsaturated β-lactam product, while the acyclic triene 1,3,5-hexatriene gave only an unsaturated amide. The proposed mechanism is initial formation of a β-lactam in a near-concerted manner followed by ring opening and reclosure to give the products.

Earlier investigations into the chemistry of chlorosulfonyl isocyanate (CSI) have examined the reactivity of CSI with olefins, dienes, tetraenes, acetylenes, and a variety of cyclic systems.[4] In our initial communication[5] we noted that the addition of CSI to 1,3,5-cycloheptatriene (**1a**) gave the 8-chlorosulfonylimino ether (**2a**) rather than a lactam product. Alkaline hydrolysis in acetone converted **2a** to the more stable lactone **3a.** In this concluding paper we report on the reaction of CSI with a number of trienes and the reactions of substituted imino ethers.

Results

Cycloheptatrienes. The 7-substituted cycloheptatrienes (**1b–e**) were synthesized via the reaction of 7-methoxy-1,3,5-cycloheptatriene with the appropriately substituted Grignard reagent.[6]

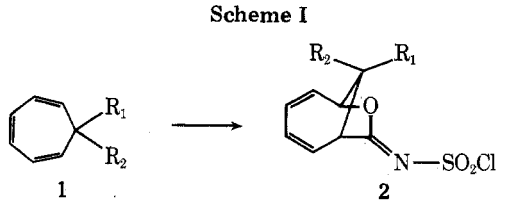
Addition of CSI to an equimolar amount of **1b** in CH_2Cl_2 at 25 °C gave the 9-methyl-8-chlorosulfonylimino ethers (**2b** and **2c**) in 85% yield and 7-methyl-1-carboxamido-1,3,5-cycloheptatriene (**4b**) in 6% yield. Alkaline hydrolysis of **2b,c** in acetone gave lactones **3b** and **3c** in 33% yield. The NMR spectrum of these lactones exhibited two methyl doublets at δ 1.40 and 0.90. The doublet at δ 0.90 was assigned to the axial methyl group (**3c**) since it was situated over the diene system and shielded relative to the equatorial methyl group (**3b**) at δ 1.40. This assignment is consistent since 7-methylcycloheptatriene (**1b**) exists as an equilibrium mixture of two conformers with the methyl group in the equatorial and axial positions.[7]

Addition of CSI to equimolar amounts of **1d** and **1e** in nitromethane followed by alkaline hydrolysis in acetone gave lactones **3d** (35%) and **3e** (20%) in which the substituent was in the axial position, i.e., over the diene system. This assignment was based on an examination of the NMR spectrum of **3d** in which the four vinyl protons appeared as two multiplets centered at δ 6.25 and 5.80 each integrating for two protons while the 7-methine proton appeared as a multiplet at δ 3.08. Therefore, because of the two two-proton vinyl multiplets and the complex multiplicity of the 7-methine proton, the substituent in **3d** and **3e** must be in the axial position and symmetrically positioned over the four vinyl protons. Interestingly, stirring CSI and **1d** in CH_2Cl_2 for 4 days followed by alkaline hydrolysis gave lactone **3d** (22%) and lactam **6g** (17%). This lactam (**6g**) arose from the prior rearrangement of **1d** to **1g** which subsequently reacted with CSI. This rearrangement of 7-substituted cycloheptatrienes was observed in the presence of other electrophilic reagents. In all the cases studied[6a] the 1 and 7 isomers were produced in greater amounts than the 2 and 3 isomers. Therefore, since the reaction of **1d** with electrophilic CSI in CH_2Cl_2 required 4 days to go to completion, the experimental conditions were such that rearrangement could have occurred prior to CSI attack.

Addition of CSI to **1f** in CH_2Cl_2 gave the *N*-chlorosulfonyllactam **5f** (62%) and alkaline hydrolysis of **5f** gave lactam **6f** (45%). Unfortunately the synthesis of **1g** gave a 45:55 mixture of **1f** and **1g** which could not be separated without causing further rearrangement.[7c] As a result the addition of CSI to **1g** followed by alkaline hydrolysis gave a mixture of lactams **6f** and **6g.** Finally the addition of CSI to **1h,** followed by alkaline hydrolysis, gave a complex mixture of isomeric lactams which could not be successfully separated.

1,5,9-Cyclododecatriene (7) (Scheme III). Addition of CSI to an equimolar amount of **7** in CH_2Cl_2 gave the *N*-chlorosulfonyl-β-lactam **8** in 80% yield. Alkaline hydrolysis of **8** in acetone gave β-lactam **9** in 49% yield. Since only one double bond in **7** had reacted with CSI, experiments were attempted to induce further addition of CSI to the β-lactam **8.** Stirring

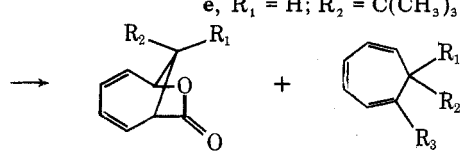
Scheme I



1 2

a, $R_1 = R_2 = H$
b, $R_1 = CH_3$; $R_2 = H$
d, $R_1 = H$; $R_2 = C_6H_5$
e, $R_1 = H$; $R_2 = C(CH_3)_3$

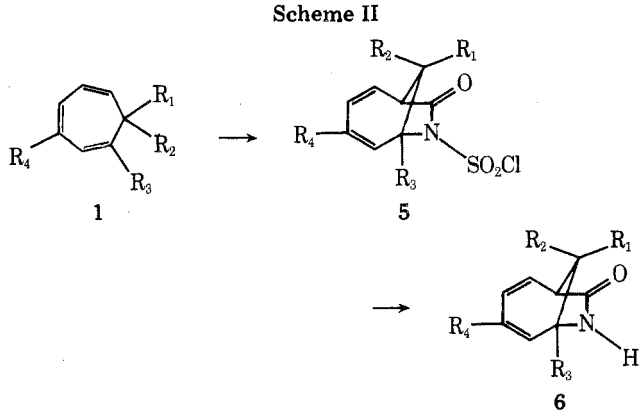
a, $R_1 = R_2 = H$
b, $R_1 = CH_3$; $R_2 = H$
c, $R_1 = H$; $R_2 = CH_3$
d, $R_1 = H$; $R_2 = C_6H_5$
e, $R_1 = H$; $R_2 = C(CH_3)_3$



3 4

b, $R_1 = CH_3$; $R_2 = H$; $R_3 = CONH_2$

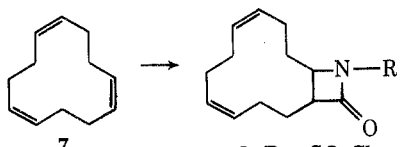
Scheme II



1 5 6

f, $R_1 = R_2 = R_3 = H$; $R_4 = C_6H_5$
g, $R_1 = R_2 = R_4 = H$; $R_3 = C_6H_5$
h, $R_1 = R_2 = R_4 = CH_3$; $R_3 = H$

Scheme III

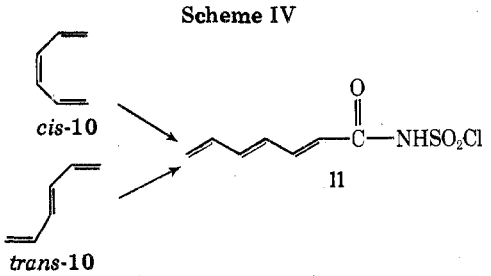


7 8, R = SO_2Cl 9, R = H

equivalent amounts of 7 and CSI at 50–55 °C in the absence of solvent for 2 h, followed by aqueous NaOH hydrolysis, gave only β-lactam **9**. When 2 equiv of CSI was stirred with 1 equiv of 7 at 50–55 °C, only 8 could be detected and no products arising from a double addition of CSI were isolated or detected spectrally.

Hexatriene (10) (Scheme IV). The procedures of Hwa and

Scheme IV



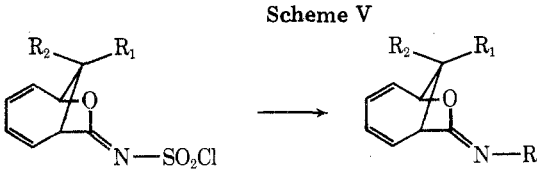
cis-10 *trans*-10 11

Sims were followed for the preparation of 1,3,5-hexatriene.[8] This method gave a mixture of cis and trans isomers which were separated by treatment with maleic anhydride.

Addition of CSI to an equimolar amount of *cis*-**10** in CH_2Cl_2 gave the *N*-chlorosulfonyl-1-carboxamido-1,3,5-hexatriene (**11**) in 18% yield. Treatment of *trans*-**10** with CSI also gave only the amide **11**.

Reaction of Imino Ethers (Scheme V). Methanolysis of

Scheme V



2 12

a, $R_1 = R_2 = H$
b, $R_1 = CH_3$; $R_2 = H$
c, $R_1 = H$; $R_2 = CH_3$

a, $R_1 = R_2 = H$; $R = SO_2OCH_3$
b, $R_1 = CH_3$; $R_2 = H$; $R = SO_2OCH_3$
c, $R_1 = H$; $R_2 = CH_3$; $R = SO_2OCH_3$
d, $R_1 = R_2 = R = H$

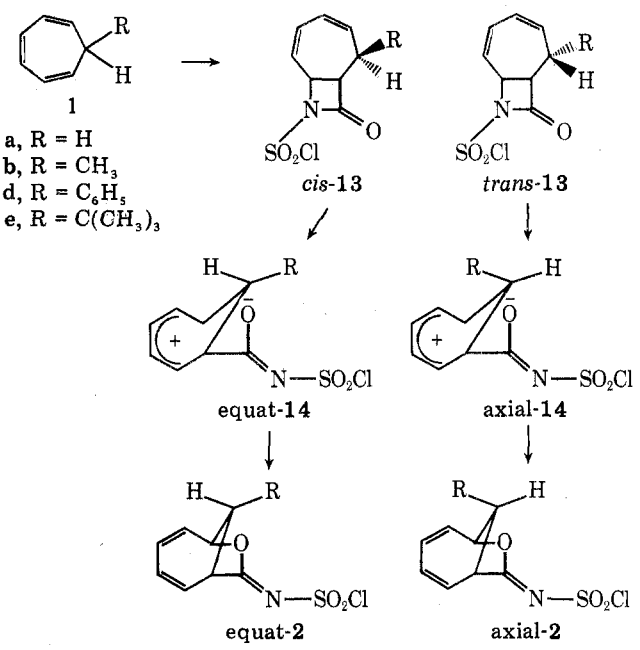
N-chlorosulfonylimino ethers **2a–c** with a saturated solution of NaOH in methanol gave the 8-methoxysulfonylimino ether **12a** (66%) and the 9-methyl-8-methoxysulfonylimino ethers (**12b** and **12c**) as an isomeric mixture (50%).

Reduction of **2a** with 1 equiv of $LiAlH_4$ in refluxing CH_2Cl_2–ether gave imine **12d** in 58% yield. Treatment of **12d** with an aqueous NaOH solution converted it quantitatively to lactone **3a**.

Discussion

The addition of CSI to cycloheptatrienes was originally postulated to be a concerted process leading to 1,2 and/or 1,6 cycloadducts.[5] However, in light of recent results of CSI additions,[9,10] this reaction involves an initial near-concerted attack to give β-lactam **13** (Scheme VI). This would represent a concerted, thermally allowed $[_\pi 2_s + _\pi 2_a]$ cycloaddition[11] in which the CSI functioned as the antarafacial component.[9b] The presence of **13** has been observed spectrally, but all attempts to isolate it were totally unsuccessful. Interestingly, the reaction of CSI with cyclooctatriene gives a stable β-lactam which eventually rearranges to other lactam products.[12] Ring

Scheme VI



1 a, R = H b, R = CH_3 d, R = C_6H_5 e, R = $C(CH_3)_3$ *cis*-13 *trans*-13 equat-14 axial-14 equat-2 axial-2

opening of β-lactam **13** gives a stable benzonium cation **14** which upon ring closure at C-6 gives the observed products.

The stereochemistry of the 7-substituted cycloheptatriene adducts can be explained via this mechanism. Since the 7-substituted cycloheptatrienes exist as equilibrium mixtures with axial and equatorial substituents,[7] then initial attack would give two β-lactams (*cis*-**13** and *trans*-**13**). Ring opening would give a 1,8-dipolar intermediate (**14**) with equatorial (equat-**14**) and axial (axial-**14**) substituents. Finally closure at C-6 would give two isomeric adducts with equatorial and axial substituents. The reaction of CSI with **1b** gave, after hydrolysis, a 45:55 mixture of isomeric lactones. On the other hand, reaction of CSI with **1d** and **1e** gave only lactones with an axial substituent (**3d** and **3e**). This result can be explained in terms of the size of these substituents. At the dipolar intermediate stage (**14**) the equatorial phenyl or *tert*-butyl group (equat-**14**) effectively blocks the attack of the oxygen atom at C-6. However when the substituent is axial (axial-**14**) there is no blockage and the oxygen can bond at C-6 to give **3d** and **3e**.

The question of nitrogen vs. oxygen closure is explained via the stabilization of the intermediate carbonium ion (**14**). In the cases where the substituent does not help to stabilize **14**, e.g., **1a–e**, then the product was the imino ether. When the substituent helps to stabilize the intermediate, e.g., **1f–h**, then the product was the lactam. Interestingly, Malpass has observed that upon prolonged standing in CCl_4, imino ether **2a** is slowly transformed via the 1,8-dipolar intermediate **14** to the corresponding lactam product.[12]

In summary, the reaction of CSI with substituted cycloheptatrienes gave only 1,6-cycloaddition products. The 7-substituted cycloheptatrienes gave only the O-cyclized adducts, while the 1- and 3-substituted cycloheptatrienes gave only the N-cyclized adducts. The mechanism involves the initial formation of a β-lactam in a near-concerted manner followed by a facile ring opening to give a 1,8-dipolar intermediate which rapidly closed to give the observed products. Finally, this mechanism represents a further example of β-lactam formation preceding rather than following the generation of a dipolar intermediate.

Experimental Section

Melting points were recorded on a Mel-Temp capillary apparatus and were uncorrected; boiling points were uncorrected. The infrared

spectra were recorded on a Perkin-Elmer 337 grating spectrophotometer. The ultraviolet spectra were taken on a Cary 15 spectrophotometer. NMR spectra were recorded on a Varian Associates A-60A and XL-100 spectrometers; chemical shifts are expressed in parts per million (δ) downfield from Me_4Si as an internal standard. Gas chromatograms were run on a Perkin-Elmer 880 instrument with a flame ionization detector and using a 6 ft × 0.125 in. stainless steel column packed with 10% SE-30 on Chromosorb W. The mass spectra were obtained at Battelle Columbus Laboratories' High Resolution Mass Spectrometry Center supported by the National Institutes of Health, Contract NIH-71-2483. Microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

Preparation of Substituted Cycloheptatrienes. Tropylium fluoroborate[6c] and 7-methoxycycloheptatriene[13] were prepared in good yield by utilizing the procedures described by Conrow.

The reaction of methylmagnesium iodine with 7-methoxycycloheptatriene gave **1b** in 60% yield, bp 50 °C (42 mm).[6a]

The reaction of phenylmagnesium bromide with 7-methoxycycloheptatriene gave **1d** in 72% yield, bp 69–71 °C (0.4 mm) [lit.[6b] 129–131 °C (12 mm)].

The reaction of *tert*-butylmagnesium chloride with 7-methoxycycloheptatriene gave **1e** in 32% yield, bp 80–82 °C (25 mm).

Reaction of CSI with Cycloheptatriene (1a). To 9.20 g (0.10 mol) of **1a** in 50 ml of CH_2Cl_2 was added dropwise a solution of 14.1 g (0.10 mol) of CSI in 25 ml of CH_2Cl_2. The reaction mixture was allowed to stir at ambient temperature for 6 h. The solvent was removed in vacuo to give a dark red oil which was crystallized from anhydrous ether to give 20.1 g (86%) of **8-chlorosulfonylimino-7-oxabicyclo[4.2.1]nona-2,4-diene (2a):** mp 86–87 °C; ir (KBr) 1600 (C=C), 1575 (C=N), 1359, 1182 cm^{-1} (SO_2); uv max (95% EtOH) 265 nm (ϵ 4400); NMR ($CDCl_3$) δ 6.18 and 6.15 (two peaks, 4, vinyl H), 5.50–5.20 (m, 1, HCO–), 4.25–3.90 (m, 1, HCC=N–), 3.05–2.25 (m, 2, $-CH_2-$).

Anal. Calcd for $C_8H_8NSO_3Cl$: C, 41.12; H, 3.45; N, 5.99. Found: C, 40.83; H, 3.68; N, 5.85.

Aqueous NaOH Hydrolysis of 2a. A solution of 9.32 g (0.04 mol) of **1a** in 150 ml of acetone and 50 ml of H_2O was cooled to −10 °C. While this temperature was maintained, 5 N NaOH was added dropwise with stirring until the solution was basic (pH 9) to litmus. Ether (50 ml) was added to the reaction mixture and the layers were separated. The aqueous layer was extracted three times with 50-ml portions of ether and six times with 50 ml of CH_2Cl_2. The organic layers were combined, dried ($MgSO_4$), and reduced in vacuo to a yellow oil. This oil was vacuum distilled at 86–88 °C (0.20 mm) to give 1.80 g (33%) of **7-oxabicyclo[4.2.1]nona-2,4-dien-8-one (3a):** ir (neat) 1760 cm^{-1} (C=O); uv max (95% EtOH) 263 nm (ϵ 4300); NMR ($CDCl_3$) δ 6.10 and 6.05 (two peaks, 4, vinyl H), 5.05–4.70 (m, 1, H_a), 3.66–3.38 (m, 1, H_b), 2.88–2.45 (m, 1, H_d), and 2.16–1.96 (d, 1, H_c, J = 12.5 Hz).

Anal. Calcd for $C_8H_8O_2$: C, 70.57; H, 5.92, mol wt, 136.0524. Found: C, 70.38; H, 5.99, mol wt, 136.0536.

Reaction of CSI with 7-Methylcycloheptatriene (1b). To 2.12 g (0.02 mol) of **1b** in 30 ml of methylene chloride was added dropwise a solution of 2.83 g (0.02 mol) of CSI in 20 ml of methylene chloride. The reaction mixture was allowed to stir overnight at ambient temperature and then poured over 25 g of ice. The water layer was extracted twice with 20 ml of methylene chloride. The combined organic layers were dried ($MgSO_4$) and concentrated in vacuo to yield 4.20 g (85%) of **9-methyl-8-chlorosulfonylimino-7-oxabicyclo[4.2.1]nona-2,4-diene** (**2b** and **2c**) as a red oil; ir (neat) 1613 (C=C), 1575 (C=N), 1368 and 1177 cm^{-1} (SO_2); NMR (CCl_4) δ 6.80–6.00 (m, 4, vinyl H), 5.30–5.00 (m, 1, HCO) 4.15–3.90 (m, 1, HCC=N), 3.20–2.70 (m, 1, –CH), 1.46–1.37 and 1.15–1.00 (two doublets, 3, CH_3 groups). The aqueous layer was extracted for 4 days with methylene chloride in a Robb extractor to yield 0.20 g (6%) of **7-methyl-1-carboxamido-1,3,5-cycloheptatriene (4b):** mp 106–107 °C; ir (KBr) 3280 and 3125 (N–H), 1600 cm^{-1} (C=O); uv max (95% EtOH) 250 nm (ϵ 2400); NMR (CD_3COCD_3) δ 7.30–7.15 (mound, 1, NH), 6.93–6.58 (m, 2, H_3, H_4), 6.32–5.90 (m, 2, H_2, H_5), 5.38–5.08 (m, 1, H_6), 1.83–1.46 (m, 1, H_7), 1.42–1.30 (d, 3, CH_3).

Anal. Calcd for $C_9H_{11}NO$: C, 72.45; H, 7.43: mol wt, 149.0841. Found: C, 71.91; H, 7.39; mol wt, 149.0818.

Aqueous NaOH Hydrolysis of 2b,c. A solution of 9.90 g (0.04 mol) of **2b,c** in 150 ml of acetone and 50 ml of H_2O was cooled to −10 °C. This solution was hydrolyzed with NaOH in a manner similar to **2a** and gave a yellow oil, which was vacuum distilled at 50–52 °C (0.10 mm) to give 2.00 g (33%) of **9-methyl-7-oxabicyclo[4.2.1]nona-2,4-dien-8-one** (**3b** and **3c**): ir (neat) 1755, 1680 cm^{-1} sh (C=O); uv max (95% EtOH) 263 nm (ϵ 4600), 256 (4700); NMR ($CDCl_3$) δ 6.10–5.50 (m, 4, vinyl H), 4.73–4.10 (m, 1, HCO–), 3.55–3.25 (m, 1, HCC=O), 2.96–2.50 (m, 1, 7-CH), 1.44–1.33 (d, 3, equatorial CH_3), 0.90–0.79 (d, 3, axial CH_3).

Anal. Calcd for $C_9H_{10}O_2$: mol wt, 150.0681. Found: mol wt, 150.0675.

Reaction of CSI with 7-Phenylcycloheptatriene (1d). To 3.40 g (0.02 mol) of **1d** in 30 ml of methylene chloride was added dropwise a solution of 2.90 g (0.02 mol) of CSI in 20 ml of CH_2Cl_2. The reaction mixture was allowed to stir for 96 h at ambient temperature. The solvent was removed in vacuo to yield a red oil. Alkaline hydrolysis of this oil in 100 ml of acetone and 30 ml of H_2O in a manner similar to **2a** afforded a red oil which was deposited on a 20 × 2.5 cm silica gel column. Elution with hexane gave 300 mg of **1d.**

Continued elution with ether–hexane (10:90) gave 920 mg (22%) of **9-phenyl-7-oxabicyclo[4.2.1]nona-2,4-dien-8-one (3d):** ir ($CHCl_3$) 1760 cm^{-1} (C=O); uv max (95% EtOH) 265 nm (ϵ 4100), 255 (4400); NMR ($CDCl_3$) δ 7.36 (s, 5, C_6H_5), 6.41–6.08 (m, 2, H_3, H_4). 5.75–5.63 (m, 2, H_2, H_5), 5.21–5.06 (m, 1, HCO–), 3.80–3.48 (m, 1, HCC=O), 3.28–2.83 (m, 1, 7-methine proton).

Anal. Calcd for $C_{14}H_{12}O_2$: mol wt, 212.0837. Found: mol wt. 212.0829.

Continued elution with ether–hexane (1:1) gave 710 mg (17%) of **6-phenyl-7-azabicyclo[4.2.1]nona-2,4-dien-8-one (6g):** ir ($CHCl_3$) 3367 (N–H), 1690 cm^{-1} (C=O); uv max (95% EtOH) 273 nm (ϵ 4700), 265 (4800); NMR ($CDCl_3$) δ 8.05 (mound, 1, NH), 7.36 (s, 5, C_6H_5), 6.31–6.08 (m, 4, vinyl H), 3.63–3.25 (m, 1, HCC=O), 2.35–2.15 (m, 2, $-CH_2-$).

Anal. Calcd for $C_{14}H_{13}NO$: C, 79.59; H, 6.20; N, 6.63; mol wt, 211.0997. Found: C, 79.42; H, 6.25; N, 6.81; mol wt, 211.0997.

Reaction of CSI with 1d in Nitromethane. To 1.68 g (0.01 mol) of **1d** in 10 ml of nitromethane was added dropwise a solution of 1.60 g (0.0113 mol) of CSI in 5 ml of nitromethane. The mixture was allowed to stir at ambient temperature for 20 h. The solvent was removed in vacuo to yield a dark red oil. This oil was hydrolyzed with 5 N NaOH in a manner similar to **2a** and afforded a yellow oil which was deposited on a 15 × 2.5 cm silica gel column. Elution with CCl_4 gave 140 mg of **1d.** Further elution with ether gave 700 mg (35%) of **3d.**

Reaction of CSI with 7-*tert*-Butylcycloheptatriene (1e). To 1.52 g (0.0103 mol) of **1e** in 10 ml of nitromethane at 0 °C was added dropwise a solution of 1.63 g (0.0115 mol) of CSI in 5 ml of nitromethane. After the addition the mixture was allowed to stir at 0 °C for 30 min and then at ambient temperature for 18 h. The solvent was removed in vacuo to give a dark red oil. Alkaline hydrolysis of this oil in 50 ml of aqueous acetone in a manner similar to **2a** afforded an oil which was deposited on a 15 × 2.5 cm silica gel column. Elution with CCl_4 gave a very small amount of **1e.**

Continued elution with $CHCl_3$ gave 385 mg (20%) of **9-*tert*-butyl-7-oxabicyclo[4.2.1]nona-2,4-dien-8-one (3e):** ir (neat) 1761 cm^{-1} (C=O); uv max (95% EtOH) 265 nm (ϵ 4300), 258 (4600); NMR ($CDCl_3$) δ 6.18–5.61 (m, 4, vinyl H), 4.12–3.98 (m, 1, HCO–), 3.80–3.37 (m, 1, HCC=O), 3.25–3.03 (m, 1, –CH–), 1.00 (s, 9, *tert*-butyl H).

Anal. Calcd for $C_{12}H_{16}O_2$: mol wt, 192.1150. Found: mol wt, 192.1129.

Preparation of 3-Phenylcycloheptatriene (1f). Under a nitrogen atmosphere, 7.00 g (0.042 mol) of **1f** was heated at 116 °C for 72 h. The reaction mixture was distilled quickly from a small flask through a Vigreux column (10 cm) at a bath temperature of 110–113 °C. Redistillation at 69–71 °C (0.03 mm) gave 6.00 g (86%) of **1f.**[7c] The NMR spectrum indicated a mixture of 92% **1f** and 8% **1g.**

Reaction of CSI with 1f. To 1.55 g (0.0092 mol) of **1f** in 20 ml of methylene chloride was added dropwise a solution of 1.52 g (0.0107 mol) of CSI in 10 ml of methylene chloride. The reaction mixture was allowed to stir for 36 h at ambient temperature and then poured over 25 g of ice and the layers separated. The aqueous layer was extracted once with 25 ml of CH_2Cl_2. The combined organic layers were dried ($MgSO_4$) and reduced in vacuo to give a yellow solid which was recrystallized from ether to yield 1.77 g (62%) of ***N*-chlorosulfonyl-4-phenyl-7-azabicyclo[4.2.1]nona-2,4-dien-8-one (5f)** as a white, crystalline solid: mp 121–122 °C; ir (KBr) 1751 (C=O), 1400 and 1175 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 7.38 (s, 5, C_6H_5), 6.63–6.25 (m, 3, vinyl H), 5.31–4.91 (m, 1, $HCNSO_2Cl$), 3.80–3.50 (m, 1, HCC=O), 2.81–2.45 (m, 1, H_{equat}), 2.20–2.00 (d, 1, J = 12.0 Hz, H_{axial}).

Anal. Calcd for $C_{14}H_{12}NSO_3Cl$: C, 54.28; H, 3.90; N, 4.52. Found: C, 54.10; H, 3.86; N, 4.55.

Aqueous NaOH Hydrolysis of 5f. Alkaline hydrolysis of 1.55 g (0.005 mol) of **5f** in 50 ml of acetone and 15 ml of H_2O in a manner similar to **2a** afforded a yellow solid which was recrystallized from ether to give 0.48 g (45%) of **4-phenyl-7-azabicyclo[4.2.1]nona-2,4-dien-8-one (6f):** mp 167–169 °C; ir (KBr) 3175 (–NH), 1666 cm^{-1} (C=O); uv max (95% EtOH) 232 nm (ϵ 10 600), 265 sh (4600); NMR ($CDCl_3$) δ 7.33 (s, 6, C_6H_5 and NH), 6.37–6.27 (m, 3, vinyl H), 4.27–3.95

(m, 1, HCN–), 3.58–3.22 (m, 1, HCC=O), 2.80–2.28 (m, 1, H_{equat}), 2.00–1.80 (d, 1, J = 12 Hz, H_{axial}).

Anal. Calcd for $C_{14}H_{13}NO$: C, 79.59; H, 6.20; N, 6.63. Found: C, 79.52; H, 6.22; N, 6.78.

Preparation of 1-Phenylcycloheptatriene (1g). Under a nitrogen atmosphere, 3.36 g (0.02 mol) of **1f** was heated at 160 °C for 14–15 h. The reaction mixture was distilled through a Vigreux column (10 cm) to yield 1.51 g (45%) of **1g**.[7c] The NMR spectrum indicated a mixture of 45% **1f** and 55% **1g**.

Reaction of CSI with 1g. To 0.84 g (0.005 mol) of **1g** (55% **1g**) in 15 ml of methylene chloride was added dropwise a solution of 0.71 g (0.005 mol) of CSI in 10 ml of methylene chloride. The reaction mixture was allowed to stir for 20 h at ambient temperature. The solvent was removed in vacuo to yield a yellow oil. Alkaline hydrolysis in acetone in a manner similar to **2a** afforded a yellow solid, infrared (KBr) 3333 (N–H), 1680 cm^{-1} (C=O). The ir and NMR spectrum indicated a mixture of lactams **6f** and **6g**.

Preparation of Eucarvone. Eucarvone was prepared by the procedures of Corey and Burke.[14] A modification of their procedures involved the use of a universal steam distillation apparatus[15] to separate the eucarvone from the other impurities. The distillate was dried (Na_2SO_4), filtered, and concentrated in vacuo to yield a yellow oil which was distilled to yield eucarvone (64%), bp 106–110 °C (20 mm) [lit.[14] bp 88 °C (10 mm)].

Preparation of 3,7,7-Trimethylcycloheptatriene (1h). The procedures of Corey, Burke, and Remers[16] were followed for the conversion of eucarvone to eucarvol which was dehydrated immediately by heating with H_2SO_4. The resulting material was distilled to yield **3,7,7-trimethyl-1,3,5-cycloheptatriene (1h),** bp 60–65 °C (20 mm) [lit.[16] 60–63 °C (20 mm)].

Reaction of CSI with 3,7,7-Trimethyl-1,3,5-cycloheptatriene (1h). To 1.35 g (0.01 mol) of **1h** in 20 ml of methylene chloride was added dropwise a solution of 1.50 g (0.0106 mol) of CSI in 10 ml of methylene chloride. The reaction mixture was allowed to stir for 5 h at room temperature. The solvent was removed in vacuo and the residue was dissolved in aqueous acetone and hydrolyzed with NaOH to give a yellow oil, infrared (neat) 1640 cm^{-1} (C=O). The NMR spectra and TLC indicated a complex mixture of lactams which could not be separated.

Reaction of CSI with 1,5,9-Cyclododecatriene (7). To 8.10 g (0.05 mol) of **7** in 50 ml of methylene chloride was added dropwise a solution of 7.21 g (0.05 mol) of CSI in 25 ml of methylene chloride. The reaction mixture was then allowed to stir at ambient temperature for 96 h and poured over 25 g of ice. The water layer was extracted four times with 25-ml portions of CH_2Cl_2. The combined organic layers were dried ($MgSO_4$), filtered, and concentrated to yield 12.2 g (80%) of ***N*-chlorosulfonyl-13-azabicyclo[10.2.0]tetradeca-4,8-dien-14-one (8)** as a clear yellow oil which could not be crystallized: ir (neat) 1818 (β-lactam C=O) 1403 and 1170 cm^{-1} (SO_2). The water layer, which was extracted on a Robb extractor for 3 days with methylene chloride, yielded no organic products.

Aqueous NaOH Hydrolysis of 8. Alkaline hydrolysis of 8 in 125 ml of aqueous acetone in a manner similar to **2a** afforded a yellow oil which was deposited on a 25 × 2.5 cm silica gel column and elution with ether gave 2.00 g (49%) of **13-azabicyclo[10.2.0]tetradeca-4,8-dien-14-one (9)** as a clear yellow liquid: ir (neat) 3236(N–H) and 1751 cm^{-1} (β-lactam C=O); uv max (95% EtOH) no absorptions above 200 nm; NMR ($CDCl_3$) δ 6.85 (broad mound, 1, NH),5.58–5.08 (m, 4, vinyl H), 3.65–3.36 (m, 1, HCNH), 3.23–2.83 (m, 1, HCC=O), 2.75–1.33 (broad peak, 12, $-CH_2-$).

Anal. Calcd for $C_{13}H_{19}NO$: mol wt, 205.1467. Found: mol wt, 205.1441.

Preparation of 1,3,5-Hexatriene (10). The procedure of Hwa and Sims[8] was followed for the preparation and separation of *cis*- and *trans*-1,3,5-hexatriene (**10**). The mixture of *cis* and *trans*-**10** was prepared in 53% yield, bp 79–81 °C (lit. bp 80–80.5 °C).

Reaction of CSI with *cis*-1,3,5-Hexatriene (10). To 0.80 g (0.01 mol) of *cis*-**10** in 20 ml of methylene chloride was added dropwise a solution of 1.41 g (0.01 mol) of CSI in 15 ml of methylene chloride. The reaction mixture was allowed to stir at ambient temperature for 8 h. The solvent was removed in vacuo to yield 0.40 g (18%) of ***N*-chlorosulfonyl-1-carboxamido-1,3,5-hexatriene (11):** ir (KBr) 1695 (amide C=O), 1380 and 1184 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 7.00–6.50 (broad mound, 1, NH), 6.16–5.83 (m, 3, vinyl H), 5.78–5.16 (m, 4, vinyl H).

Alkaline Hydrolysis of *N*-Chlorosulfonyl Imino Ethers in Methanol. The general procedure used was as follows. A solution of **2** in acetone was treated with a saturated solution of NaOH in absolute CH_3OH to pH 9 at 0 °C. Sufficient water was added to clarify the reaction mixture which was extracted with five 50-ml portions of CH_2Cl_2. The combined extracts were dried ($MgSO_4$) and filtered and the solvent was removed in vacuo. The resulting residue was deposited on a 20 × 2.5 cm silica gel column and eluted with ether to give a methoxy ester.

8-Methoxysulfonylimino-7-oxabicyclo[4.2.1]nona-2,4-diene (12a) was obtained from **2a** (66%): ir ($CHCl_3$) 1645 (C=N), 1364 and 1160 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 6.20 (broad single peak, 4, vinyl H), 5.43–5.05 (m, 1, HCO), 4.45–4.00 (m, 1, HCC=N), 3.91 (s, 3, $-OCH_3$), 3.05–2.51 (m, 1, H_{equat}), 2.40–2.20 (d, 1, J = 12.5 Hz, H_{axial}); mass spectrum *m/e* (rel intensity) 135 (4.99), 117 (11.88), 92 (22.59), 91 (47.34), 65 (33.90), 63.96 (100.00).

9-Methyl-8-methoxysulfonylimino-7-oxabicyclo[4.2.1]nona-2,4-diene (12b,c) was obtained from **2b,c** (49%); ir ($CHCl_3$) 1619 (C=N), 1340 and 1170 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 6.30–6.00 (m, 4, vinyl), 5.30–5.00 (m, 1, HCO), 4.15–3.90 (m, 1, HCC=N), 3.86 (s, 3, OCH_3), 3.03–2.61 (m, 1, –CH), 1.46–1.37 and 1.15–1.00 (two doublets, CH_3).

Anal. Calcd for $C_{10}H_{13}NO_4S$; mol wt, 243.0565. Found: mol wt, 243.0594.

Lithium Aluminum Hydride Reduction of 2a. To a slurry of 0.40 g (0.01 mol) of $LiAlH_4$ in 20 ml of anhydrous ether was added a solution of 2.30 g (0.01 mol) of **2a** in 40 ml of CH_2Cl_2. The mixture was refluxed for 15–20 min and then treated with successive addition of 0.5 ml of H_2O, 0.5 ml of 15% NaOH, and 1.5 ml of H_2O. The resulting solid was filtered and washed with 25 ml of ether. The combined filtrates were dried ($MgSO_4$), filtered, and concentrated in vacuo to yield 0.78 g (58%) of **8-imino-7-oxabicyclo[4.2.1]nona-2,4-diene (12d):** ir (neat) 3300 (C=N—H) and 1666 cm^{-1} (–C=N).

Registry No.—**1a,** 544-25-2; **1b,** 4281-04-3; **1d,** 1541-11-3; **1e,** 17635-75-5; **1f,** 1541-13-5; **1g,** 1541-14-6; **1h,** 3479-89-8; **2a,** 28000-12-6; **2b,** 59938-81-7; **2c,** 59938-82-8; **3a,** 28000-13-7; **3b,** 59938-83-9; **3c,** 59938-84-0; **3d,** 59938-85-1; **3e,** 59938-86-2; **4b,** 56771-82-5; **5f,** 59938-87-3; **6f,** 59938-88-4; **6g,** 59938-89-5; **7,** 4904-61-4; **8,** 59938-90-8; **9,** 59938-91-9; *cis*-**10,** 2612-46-6; **11,** 59938-92-0; **12a,** 59938-93-1; **12b,** 59938-94-2; **12c,** 59938-95-3; **12d,** 59938-96-4; CSI, 1189-71-5.

References and Notes

(1) (a) The support of this work by Public Health Service Research Grant 5 R01 A108063-01-03, from the National Institute of Allergy and Infectious Diseases, is gratefully acknowledged. (b) Taken entirely from the Ph.D. Thesis of C. F. Hummel, Fordham University, 1973.
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