Diethyl 9-Nitro-3-oxo-2,4-diazabicyclo[3.3.1]non-6-ene-6,8-dicarboxylate (12). A mixture of 1 (1.41 g, 10 mmol) and diethyl 1,3-acetonedicarboxylate (2.02 g, 15 mmol) in 95% ethanol (30 mL) containing two drops of 1 N HCl was heated at reflux for 30 h. The solvent was removed in vacuo and the residue was chromatographed over a column of silica gel (Woelm 70-230 mesh, 30 × 3 cm), using chloroform as the eluent. From the major UV absorbing fraction, 1.37 g (40%) of **12** was obtained: mp 149-150 °C dec; UV (H_2O) λ_{max} 252 nm (ϵ 7210); ^1H NMR δ 1.21 (3 H, t, CH_2CH_3), 1.31 (3 H, t, CH_2CH_3), 3.67 (1 H, d, H8, exchangeable, $J_{1,8}$ = 2.1 Hz), 4.16 (2 H, q, CH_2CH_3), 4.19 (2 H, q, CH_2CH_3), 4.50 (1 H, m, H1), 4.78 (1 H, m, H5) 5.17 (1 H, narrow m, H9), 6.94 (1 H, d, NH, exchangeable), 7.33 (1 H, d, NH, exchangeable), 12.0 (1 H, s, enolic OH, exchangeable).

Anal. Calcd for $C_{13}H_{17}N_3O_8 \cdot 0.5H_2O$: C, 44.32; H, 5.15; N, 11.93. Found: C, 44.55; H, 4.98; N, 12.04.

***p*-Nitrophenol (3) from Compound 2.** A solution of **2** (200 mg, 1 mmol) in 1 N NaOH (30 mL) was stirred at room temperature for 5 h. The dark-yellow solution was cooled in an ice bath and then acidified with 6 N HCl to pH ~2. The solution was extracted with ether (3 × 40 mL). The ether extracts were dried and evaporated, and the residue was crystallized from water to give 118 mg (85%) of **3**, mp 112-113 °C. A mixture of this material with an authentic sample showed no depression of the melting point. The IR and UV absorption spectra were identical in every detail with that of an authentic sample.

In a similar manner, **3** was obtained from **5** and **6** in quantitative yield. Compounds **7** and **8** were converted into 4-nitrocresol **9**: mp 93-94 °C (lit.[25] mp 93-94 °C); UV λ_{max} 229 nm (ϵ 6600), 325 (9200), λ_{min} 257 (1000); ^1H NMR δ 2.20 (3 H, s, CH_3), 6.94 (1 H, s, H6), 7.93 (1 H, dd, H5), 8.03 (1 H, d, H3).

Anal. Calcd for $C_7H_7NO_3$: C, 54.90; H, 4.61; N, 9.15. Found: C, 54.97; H, 4.64; N, 8.99.

5-Nitrosalicylic Acid (11) from Adduct 10. A solution of **10** (259 mg, 1 mmol) in 1 N NaOH (30 mL) was stirred for 5 h at room temperature. Upon acidification of the mixture with 6 N HCl to pH ~2, 5-nitrosalicylic acid (**11**) precipitated. Recrystallization of the precipitate from water gave pure **11**: 130 mg (70%), mp 228-229 °C (lit.[26] mp 228-229 °C); UV λ_{max} 219 nm (ϵ 13500), 250 (sh) (4500), 315 (9500), λ_{min} 268 (2600); ^1H NMR δ 7.16 (1 H, d, H3, $J_{3,4}$ = 9.2 Hz), 8.34 (1 H, dd, H4, $J_{3,4}$ = 9.2, $J_{4,6}$ = 2.8 Hz), 8.57 (1 H, d, H6, $J_{4,6}$ = 2.8 Hz).

Anal. Calcd for $C_7H_5NO_5$: C, 45.91; H, 2.75; N, 7.65. Found: C, 45.99; H, 2.84; N, 7.63.

In a similar manner, 2-hydroxy-5-nitroisophthalic acid (**13**) was prepared from **12**, 138 mg (61%) mp 209-210 °C (lit.mp 213-214 °C); UV λ_{max} 216 nm (ϵ 17600), 325 (14700), λ_{min} 274 (3900); ^1H NMR δ 8.68 (s, H4, 6).

Anal. Calcd for $C_8H_5NO_7$: C, 42.31; H, 2.22; N, 6.17. Found: C, 42.45; H, 2.36; N, 6.38.

Registry No. 1, 23938-66-1; 2, 79918-37-9; 3, 100-02-7; 4, 17758-39-3; 5, 79918-38-0; 6, 79918-39-1; 7, 79918-40-4; 8, 79918-41-5; 9, 99-53-6; 10, 79918-42-6; 11, 96-97-9; 12, 79918-43-7; 13, 67294-53-5.

(25) *Beilstein* **1923**, *6*, 336.
(26) *Beilstein* **1927**, *10*, 116.
(27) *Beilstein* **1927**, *10*, 502.

Intramolecular Diels-Alder Cycloadditions of Perchloro(allyloxy)- and Perchlorobis(allyloxy)cyclopentadienes[1]

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The intramolecular cycloadditions of some mono(allyloxy)- and bis(allyloxy)perchlorocyclopentadienes have been carried out. Even in the case of trisubstituted olefins, this internal cycloaddition process occurs in good yield. The allyloxy compounds (**10**, **11**, **15**, and **16**) were prepared by treating hexachlorocyclopentadiene (**9**) with the corresponding allylic alcohol in basic solution. In only one case could the intermediate allyloxy diene be isolated (compound **16**), the normal process being an in situ internal Diels-Alder reaction to produce the bridged cycloadducts (**12**, **13**, **17**, and **18**) in good yield. The structures of the adducts were determined by a combination of chemical and spectroscopic means. Acidic hydrolysis of the adducts **13** and **18** produced the corresponding hydroxy ketones **8** and **19**, respectively, in high yield. NMR analysis of the adducts also confirmed the assigned structures. By the use of double-resonance and nuclear Overhauser effects, nearly all of the resonances could be assigned and the coupling constants determined. Finally, an unsuccessful attempt to apply these results to the total synthesis of the sesquiterpene β-cuparenone (**4**) is also described.

We have recently reported on the usefulness of dimethoxytetrachlorocyclopentadiene (**1**) in Diels-Alder reactions with both electron-rich and electron-poor dienophiles in a three-carbon annulation process.[3] The adducts could also serve as substrates for anionic oxy-Cope rearrangements[4] with aromatic systems in the preparation of steroid analogues[5] and in the total synthesis of coronafacic acid.[6] However, although this diene **1** is quite reactive with mono- and disubstituted olefins as dienophiles, it is very unreactive when the dienophile is tri- or tetrasubstituted. For example, the cycloaddition of **1** with isobutenyl acetate (**2**) required refluxing in neat **2** (bp 131 °C) for 3-4 weeks.[7] The adducts **3**, which could be taken on to β-cuparenone (**4**), were formed in only 38% yield in the cycloaddition process.[7] Because of these very severe conditions necessary to effect a reaction between the diene **1** and a trisubstituted olefin and because of the poor yields of adducts obtained, it was decided to investigate the possibility of performing intramolecular Diels-Alder reactions on 5-monosubstituted and 5,5-disubstituted per-

(1) Presented at the 14th Sheffield Stereochemistry Conference, Sheffield, England Dec 1980.
(2) Camille and Henry Dreyfus Teacher-Scholar, 1978-1983. Fellow of the Alfred P. Sloan Foundation, 1979-1981.
(3) Jung, M. E.; Hudspeth, J. P. *J. Am. Chem. Soc.* **1977**, *99*, 5508.
(4) Evans, D. A.; Golob, A. M. *J. Am. Chem. Soc.* **1975**, *97*, 4765.
(5) Jung, M. E.; Hudspeth, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 4309.
(6) Jung, M. E. Hudspeth, J. P. *J. Am. Chem. Soc.* **1980**, *102*, 2463.
(7) Jung, M. E.; Radcliffe, C. D. *Tetrahedron Lett.* **1980**, 4397.

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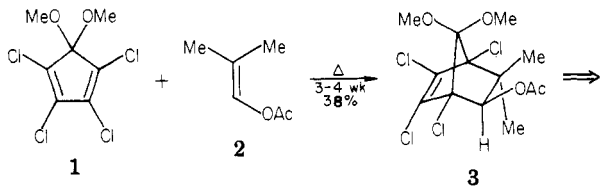
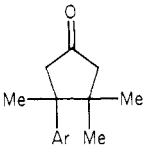


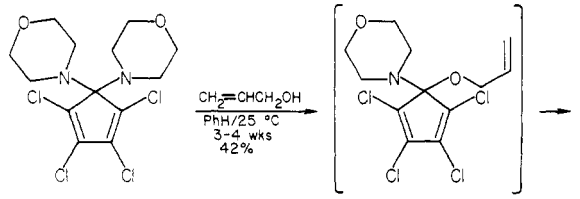


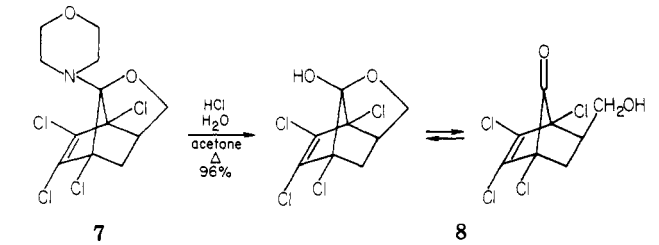
4, Ar = *p*-tolyl

chlorocyclopentadienes in which the substituents contained olefinic units. We now report our results in this area.

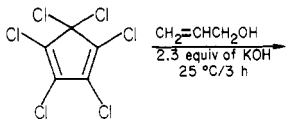
Results and Discussion

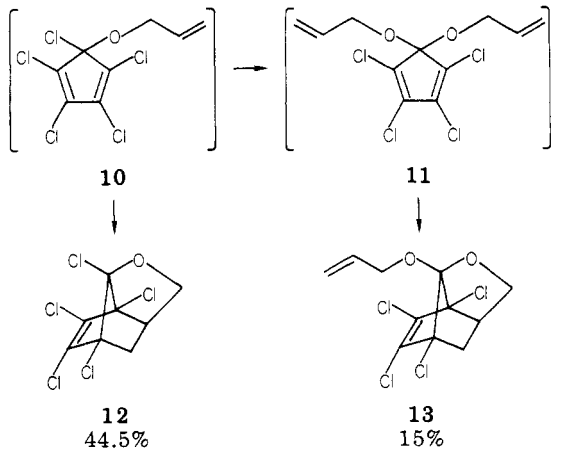
Intramolecular Diels–Alder Reactions. The first thorough investigation of the reactivity of the diene **1** in Diels–Alder reactions was carried out by McBee.[8] Later McBee reported that keeping a solution of excess allyl alcohol and 5,5-dimorpholinyltetrachlorocyclopentadiene (**5**) in benzene at 25 °C for 4 weeks produced the adduct **7** presumably by way of the (allyloxy)morpholino diene **6**.[9] Hydrolysis of **7** afforded the keto alcohol **8** which exists predominantly in the keto form in solution but in the hemiketal form as the solid.[9] Besides this brief report, no other intramolecular cycloadditions of perchlorocyclopentadiene derivatives have been described.





We decided that the morpholino group was an unnecessary complication and that the Diels–Alder reaction could be made to occur with simpler substrates, for example, the simple allyloxy-substituted perchlorocyclopentadiene. In general, 5,5-dialkoxytetrachlorocyclopentadienes, such as **1**, are prepared by the reaction of hexachlorocyclopentadiene (**9**) with the corresponding alcohol in the presence of potassium hydroxide. When a solution of **9** in allyl alcohol was treated with 2.3 equiv of potassium hydroxide for 3 h at 25 °C, neither the corresponding 5-(allyloxy)pentachlorocyclopentadiene (**10**) nor the 5,5-bis(allyloxy)tetrachlorocyclopentadiene (**11**) was isolated after workup. Instead separation of the reaction products by chromatography afforded 44.5% of the pentachloro adduct **12** and 15% of the tetrachloro adduct **13**, along with 8% recovered hexachlorocyclopentadiene (**9**) and an unidentified ketone **14**. The adducts are presumably formed by internal cycloaddition of the mono(allyloxy)- and bis(allyloxy)perchlorocyclopentadienes, **10** and **11**, respectively. It is interesting to note that these cycloadducts are formed under quite mild conditions (25 °C, 3 h) compared to those of normal cycloadditions of dimethoxytetrachlorocyclopentaidene (**1**; reflux, 48 h).[8] Obviously, the intramolecularity of the cycloaddition allows it to proceed very readily.



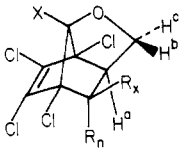


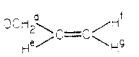
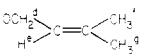
There is an alternative mechanism possible for the production of **12** and **13**, namely, an initial Diels–Alder reaction of **9** and allyl alcohol to product the exo cycloadduct the hydroxyl group of which would then displace internally a chlorine atom from the bridge carbon to give **12** and thence **13**. This mechanism can be easily ruled out since the Diels–Alder reaction of **9** with allyl alcohol is known to produce only the endo rather than the exo cycloadduct in high yield.[10] The possibility that the reaction gives initially the endo cycloadduct which equilibrates with the exo isomer (via a retro-Diels–Alder reaction or some other process) and that the latter is then trapped by internal alkylation seems highly unlikely.

With the successful accomplishment of an intramolecular Diels–Alder reaction of (allyloxy)perchlorocyclopentadiene under very mild conditions, attention was then directed to internal cycloadditions of more hindered olefins, e.g., tri- and tetrasubstituted olefins, to determine if the very sluggish reactivity of **1** toward such olefins mentioned earlier could be overcome by intramolecularity. Stirring a solution of hexachlorocyclopentadiene (**9**) with 2.3 equiv of potassium hydroxide in 3,3-dimethylallyl alcohol for 9 h at 25 °C produced a mixture of products. Chromatographic separation afforded four major products, namely, the 5,5-bis[(dimethylallyl)oxy]tetrachlorocyclopentadiene (**16**; 15%), the pentachloro cycloadduct **17** (12%), the (dimethylallyl)oxy cycloadduct **18** (31%), and another unidentified ketone **19**. No [(dimethylallyl)oxy]pentachlorocyclopentadiene (**15**) was present in the product mixture. Again it is assumed that the adducts **17** and **18** are formed by the internal cycloaddition of the cyclopentadienes **15** and **16**, respectively. This premise

(8) McBee, E. T.; Diveley, W. R.; Burch, J. E. *J. Am. Chem. Soc.* **1955**, *77*, 385.
(9) McBee, E. T.; Stoffer, J. O.; Braendlin, H. P. *J. Am. Chem. Soc.* **1962**, *84*, 4540.
(10) (a) Fields, E. K. *J. Am. Chem. Soc.* **1954**, *76*, 2709. (b) Claisse, J. A.; Davies, D. F. *J. Chem. Soc. B* **1967**, 679.

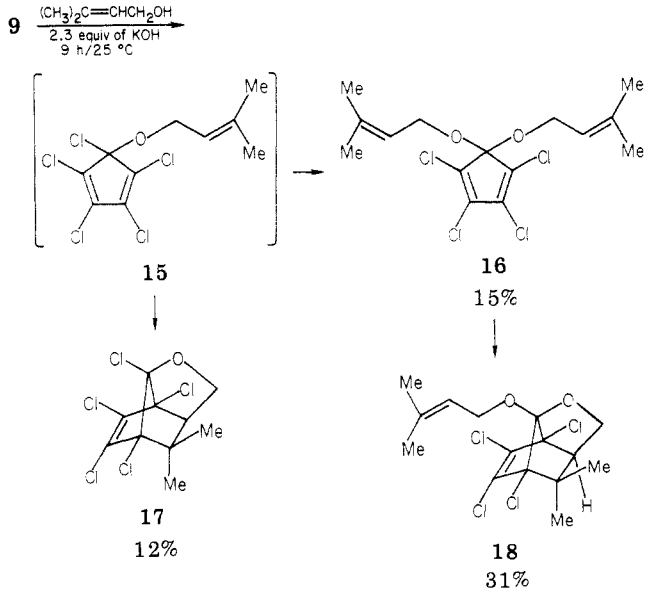
Table I. ^{1}H NMR Data of Cycloadducts



	12 X = Cl R = H^h	13 X =  R = H^h	17 X = Cl R = CH$_3$ ^{h}	18 X =  R = CH$_3$ ^{h}
		Chemical Shift[a] and Multiplicity		
H^a	2.25-2.29 (m)	2.06-2.22 (m)	2.184 (d)	2.000 (d)
H^b	4.312 (br d)	4.214 (dd)	4.438 (d)	4.321 (d)
H^c	4.745 (d)	4.638 (dd)	4.724 (dd)	4.578 (dd)
H^d		4.510 (AB_q of m)		4.487 (bm)
H^e		5.879 (ddt)		5.288 (bm)
H^f		5.301 (ddt)		1.721 (s)
H^g		5.149 (ddt)		1.636 (s)
H^h_x	2.25-2.29 (m)	2.06-2.22 (m)	1.382 (s)	1.327 (s)
H^h_n	2.724 (m)	2.559 (m)	0.971 (s)	0.872 (s)
		Coupling Constants[b]		
J_{ab}	0	0	0	0
J_{ac}	~0.5	~0.5	1.6	1.6
J_{bc}	7.8	7.8	8.5	8.8
J_{de}		5.1		
J_{df}		1.7		
J_{dg}		1.5		
J_{ef}		17.1		
J_{eg}		10.5		
J_{fg}		1.7		

[a] Determined on a Bruker WP-200 NMR spectrometer in deuteriochloroform and reported in parts per million downfield from internal tetramethylsilane. [b] Measured in hertz, determined either directly or by double-resonance experiments.

could be directly tested in this case, since **16** could be isolated. Letting **16** stand at 5 °C for an extended period or refluxing in benzene for 2 h effected its conversion into **18**.



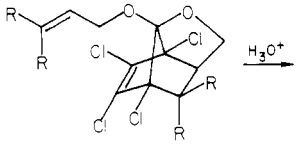
It is interesting that this enormous difference in reaction rates between the intramolecular Diels–Alder reaction of **9** with dimethylallyl alcohol (9 h, 25 °C, 43%) and the intermolecular cycloaddition of **1** and **2** (3–4 weeks, 131 °C, 38%) is observed even though there is considerable ring strain in the products of the intramolecular case. As expected, even though both are intramolecular, the cycloaddition of **10** and **11** to give **12** and **13** occurs more readily than the cycloaddition of **15** and **16** to give **17** and **18**, presumably due to the increased steric hindrance in the dimethyl case. The variation in the ratio of the cyclized products in the two cases (**12**/**13** = 45:15; **17**/**18** = 12:31) can also be easily explained by this difference in the rates of the two intramolecular cycloadditions. Presumably mono(allyloxy)pentachlorocyclopentadiene (**10**) formed initially can undergo cycloaddition very rapidly since it is relatively unhindered and thus a large amount of **12** is produced at the expense of **13**. On the other hand, the corresponding [(dimethylallyl)oxy]pentachlorocyclopentadiene (**15**) does not cyclize very readily and thus is converted in greater part to the bis[(dimethylallyl)oxy] compound **16**, with the result that the amount of **18** produced exceeds that of **17**.

Structure Determination and Reactions of the Adducts. The structures of all of the adducts were determined by a combination of spectroscopic data and chemical transformations. The ^{1}H NMR spectra of the adducts are given in Table I. In the allyloxy compounds **12** and **13**, the two protons of the bridging methylene unit (H^b, H^c) are separated by slightly more than 0.4 ppm and are significantly coupled. One (H^c) is coupled additionally to the vicinal methine proton (H^a), but the other (H^b) is essentially unsplit by this proton (H^a). The same pattern generally holds true for the (dimethylallyl)oxy compounds **17** and **18**, although there are some small differences. In particular, the coupling constants of the three-spin system have changed slightly. While the geminal protons (H^b, H^c) are still strongly coupled, neither is split significantly by the methine proton H^a, with J_{ab} = 0 and J_{ac} = 1.6 Hz. The reasons for these two very small coupling constants are not clear at this time.

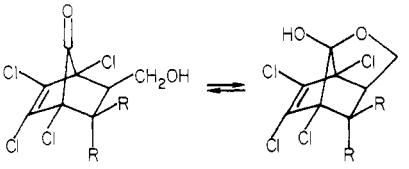
Comparison of the resonances for the methine proton (H^a) in compounds **17** and **18** indicates that this is another instance of the recently described W effect on proton chemical shifts.[11] In both compounds the methine proton (H^a) has a W relationship with the group X on the bridge carbon. When this group is chlorine (compound **17**), the proton resonates almost 0.2 ppm downfield of its resonance when this group is (dimethylallyl)oxy (compound **18**). Obviously the more electronegative chlorine atom affects this proton via the W relationship more than does the less electronegative alkoxy function. One also observes this W effect by comparing the chemical shifts of the protons of compounds **12** and **13**. Again the resonance of the methine proton (H^a) in adduct **12** is shifted downfield of that in compound **13**, although this proton is not well separated from the other protons in the molecule.

The assignment of the resonances of H^b and H^c and of the resonances for the *exo*- and *endo*-methyl groups (H^h_x and H^h_n, respectively) in the adduct **17** was made by use of nuclear Overhauser effects (NOE). Irradiation of the upfield methyl resonance (δ 0.971) in the NMR spectrum of **17** caused a significant increase (>9%) in the methine resonance at δ 2.184 (H^a) with essentially no other effect on the resonances for H^b and H^c. Thus this methyl group must be endo (H^h_n). On the other hand, irradiation of the downfield methyl resonance (δ 1.382) caused a substantial increase (>16%) in the resonance at δ 4.438 (with no effect on H^a or H^c), thereby implying that this methyl group must be exo (H^h_x) and the resonance at δ 4.438 must be due to H^b. The assignment of resonances in the other adducts—**12**, **13**, and **18** —was made by analogy to those in **17**.

To guarantee the overall structure of the adducts **13** and **18**, we hydrolyzed the adducts to the corresponding hydroxy ketones **8** and **19** under strongly acidic conditions.



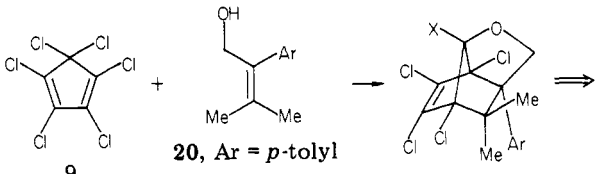
13, R = H
18, R = Me



8, R = H (82%)
19, R = Me (88%)

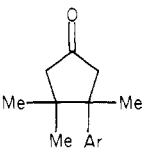
Compound **8** was shown to be identical with an authentic sample prepared by the method of McBee[9] mentioned earlier. The ^1H NMR of **8** indicates that in chloroform solution, this compound exists mainly in the hemiketal form, although the infrared spectrum (taken as a solution in methylene chloride) shows a very weak band for the ketone of the keto form (1820 cm^{-1}). In contrast the dimethyl analogue **19** exists as an approximately 1:1 mixture of the keto and hemiketal form in chloroform solution, again as indicated by the ^1H NMR.

Synthetic Approach to β-Cuparenone (4). Our success in carrying out an intramolecular Diels–Alder reaction with a trisubstituted olefin prompted us to test the possibility of carrying out an analogous reaction with a tetrasubstituted olefin. In particular, we hoped to be able to induce the alcohol **20** to react with hexachlorocyclopentadiene (**9**) to give either of the adducts **21a** and **21b**. The facile production of these compounds would open up the possibility of a very rapid and efficient synthesis of the sesquiterpene β-cuparenone **4** by application of a modification of our three-carbon annulation process and eventual reduction of the hydroxymethyl group to a methyl.



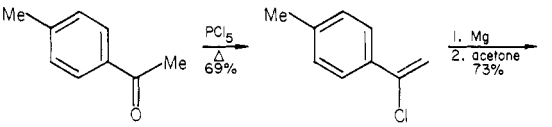
9 **20**, Ar = *p*-tolyl

21a, X = Cl
21b, X = OR

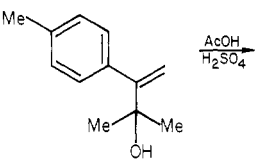


4

The necessary alcohol **20** could be prepared in four steps from commercially available *p*-methylacetophenone (**22**) in 38% overall yield. The ketone **22** was first converted into the known vinyl chloride **23** by reaction with phosphorus pentachloride.[12] Formation of the Grignard



22 **23**



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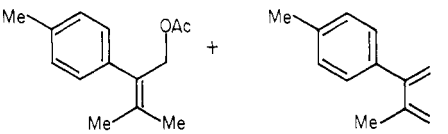
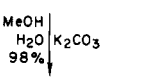
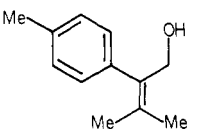


25 (78%) **26** (12%)





20

reagent of **23** followed by addition of acetone produced the tertiary allylic alcohol **24**. Rearrangement to the desired primary allylic alcohol **21** was accomplished by the two-step procedure via the acetate **25** since this route normally gives higher yields of clean products than simple rearrangement.[13] Stirring a solution of the alcohol **24** in acetic acid/sulfuric acid produced a mixture of two compounds which could be separated by preparative HPLC to give 78% of the acetate **25** and 12% of the butadiene **26**. Basic

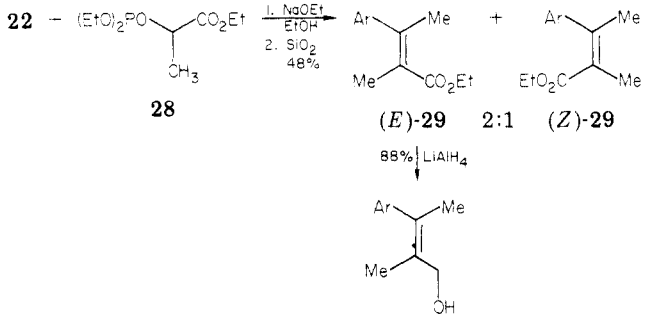
(11) Jung, M. E.; Shapiro, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 7862.

(12) Smith, L. I.; Hoehn, H. H. *J. Am. Chem. Soc.* **1941**, *63*, 1175.

(13) For another example of the use of this two-step procedure for rearrangement, see: Jung, M. E.; McCombs, C. A. *J. Am. Chem. Soc.* **1978**, *100*, 5207.

hydrolysis of the acetate **25** afforded the desired alcohol **20** in 98% distilled yield. However, when 1 equiv of hexachlorocyclopentadiene (**9**) was treated with 2.3 equiv of potassium hydroxide in 25 equiv of the alcohol **20**, none of the desired cycloadducts **21a** and **21b** were obtained. Indeed no products derived from hexachlorocyclopentadiene (**9**) could be isolated, not even the corresponding tetrachloro ketal, the only isolable product being a trace of the diene **26**. Presumably, the alcohol **20**, even though primary, is too hindered to attack hexachlorocyclopentadiene (**9**) so that no monoalkoxy- or dialkoxyperchlorocyclopentadienes are formed and there is never a chance for the intramolecular cycloaddition. It is known that very hindered alcohols, e.g., *tert*-butyl alcohol, do not produce the corresponding dialkoxytetrachlorocyclopentadienes when reacted with **9**. Thus this simple approach to β-cuparenone (**4**) failed at this point.

In order to try to overcome some of the steric encumbrance of the alcohol used for reaction with **9** and still produce intermediates of use for the synthesis of **4**, we decided to prepare the *E* alcohol **27**. The ketone **22** was reacted with the phosphonate **25**[14] to furnish a 2:1 mixture of the *E* and *Z* esters (*EZ*)-**29**, which could be readily separated by HPLC.[15] Reduction of the *E* ester **29** with lithium aluminum hydride afforded the desired alcohol **27** in good yield. However, as before, reaction of the diene **9** and potassium hydroxide in a solution of the alcohol **27** gave none of the desired adducts. Again no products derived from hexachlorocyclopentadiene could be isolated. The alcohol is once more presumably too hindered to react with the diene **9** and thus no mono- or dialkoxyperchloro dienes were produced.



When the schemes described above and several other attempts also failed,[17] it was decided to discontinue work on this system. Thus, while the intramolecular cycloaddition of a trisubstituted olefin has been successfully accomplished, the analogous reaction of a tetrasubstituted olefin has not due to our inability to prepare the desired substrate. However, intramolecular reactions to produce compounds analogous to **12**, **13**, **17** and **18** should be of value in organic synthesis.

Experimental Section

General Procedures. Melting points were determined on a Büchi capillary melting point apparatus and were corrected. Infrared spectra were recorded on a Perkin-Elmer Model 137 spectrometer either as a neat liquid film or in chloroform or dichloromethane solution and are so labeled. Nuclear magnetic resonance spectra were taken on a Varian Model T-60 or a Bruker WP-200 spectrometer and are appropriately labeled. The spectra are reported in parts per million downfield from internal tetramethylsilane. Low- and high-resolution mass spectra were recorded on an AEI MS-9 instrument.

High-pressure liquid chromatography experiments were performed on a Waters Associates Prep LC/System 500. Column chromatography was performed on Merck silica gel 60 (70–230 mesh) or Merck aluminum oxide 90 (neutral, activity adjusted with water).

Diethyl ether and tetrahydrofuran were distilled from sodium and benzophenone. Ethanol was distilled from sodium, and acetone was dried over calcium sulfate and distilled. Other reagents were purified according to literature methods.

1-Chloro- and 1-(Allyloxy)-6,7,8,9-tetrachloro-2-oxatricyclo[4.3.0.0^{4,9}]non-7-ene (12 and 13). Powdered potassium hydroxide (0.945 g, 16.8 mmol) dissolved in 7.5 mL of allyl alcohol was added dropwise to a solution of 2.0 g (7.32 mmol) of hexachlorocyclopentadiene (**9**) in 10 mL of allyl alcohol at 0 °C under an atmosphere of nitrogen. The brownish solution was warmed to 25 °C for 3 h, ice water was added, the layers were separated, and the aqueous phase was extracted 3 times with 40 mL of dichloromethane. The combined organic layers were dried over sodium sulfate and evaporated to give 2.22 g of a yellow oil. The crude infrared spectrum indicated that a carbonyl-containing impurity was produced in the reaction (1740 cm^{-1}). This impurity was separated by chromatography on activity II alumina, using pentane as eluent, and the remaining material was separated by high-pressure liquid chromatography, using a Waters Prep 500 and 5% ethyl acetate in hexane as solvent. This produced 952 mg of the cyclized chloro compound **12** (44.5%) and 345 mg of the cyclized allyloxy compound **13** (15%).

Compound **12**: white crystals; mp 62–63 °C; NMR, see Table I; IR (50 mg/mL solution in $CHCl_3$) 2930, 1600, 1110, 1070 cm^{-1}; high-resolution mass spectrum calcd for $C_8H_5OCl^{35}{}_3Cl^{37}$ 258.9065, found *m/e* 258.9059 (M^+ – Cl), calcd for $C_8H_5OCl^{35}{}_4$ 256.9095, found *m/e* 256.9096 (M^+ – Cl); mass spectrum, *m/e* 296, 294, 292, (M^+), 263, 261, 259 (base), 257 (M^+ – Cl), 231, 229 (M^+ – CO – Cl), 198, 197, 196, 195, 194, 193 [M^+ – CO, –2HCl (–H)].

Compound **13**: oil; NMR, see Table I; IR (liquid film) 3000–2825, 1600, 1440, 1270, 1230, 1110, 1060, 1030, 990, 945, 920, 820 cm^{-1}; High-resolution mass spectrum calcd for $C_8H_5OCl^{35}{}_3Cl^{37}$ 258.9065, found *m/e* 258.9065 ($M^+ - OCH_2CH{=}CH_2$), calcd for $C_8H_5OCl^{35}{}_4$ 256.9095, *m/e* 256.9095 ($M^+ - OCH_2CH{=}CH_2$); mass spectrum, *m/e* 263, 261, 259, 257 ($M^+ - OCH_2CH{=}CH_2$), 233, 231, 229 ($M^+ - OCH_2CH{=}CH_2$, –CO), 198, 197, 196, 195, 194, 193 [M^+ – CO, –HCl, $-HOCH_2CH{=}CH_2$ (–H)].

1-Chloro- and 1-[(Dimethylallyl)oxy]-6,7,8,9-tetrachloro-5,5-dimethyl-2-oxatricyclo[4.3.0.0^{4,9}]non-7-ene (17 and 18). Powdered potassium hydroxide (0.381 g, 6.79 mmol) dissolved in 3.6 g of dimethylallyl alcohol was added dropwise to a solution of hexachlorocyclopentadiene (**9**; 0.77 g, 2.82 mmol) in 4.9 g of dimethylallyl alcohol at 0 °C under an atmosphere of nitrogen. The reaction mixture was warmed to 25 °C for 9 h, ice water was added, the layers were separated, and the aqueous phase was extracted with dichloromethane. The combined organic layers were washed with brine, dried over sodium sulfate, and evaporated to give 8 g of a yellow oil. The starting alcohol was removed by vacuum distillation and the residue was chromatographed, first on activity II alumina, using pentane as eluent to remove carbonyl containing impurities (IR 1745 cm^{-1}), and then on silica gel with 8% diethyl ether in hexane to separate the products. This afforded 108 mg (12%) of the cyclized chloro compound **17** as a crystalline solid, 324 mg (31%) of the cyclized (dimethylallyl)oxy compound **18** as colorless needles, and 156 mg (15%) of the uncyclized bis(dimethylallyl) ketal **16** as an oil.

Compound **17**: mp 134–137 °C; NMR, see Table I; IR (liquid film) 2920, 1600, 1400, 1380, 1130, 1100, 1090, 1070 cm^{-1}; High-resolution mass spectrum calcd for $C_{10}H_9OCl^{35}{}_3Cl^{37}$ 286.9378, found *m/e* 286.9376 (M^+ – Cl), calcd for $C_{10}H_9OCl^{35}{}_4$ 284.9408, found *m/e* 284.9407 (M^+ – Cl); mass spectrum, *m/e* 291, 289, 287, 285 (base, M^+ – Cl), 253, 251, 249, 247 (M^+ – Cl, –HCl), 226, 225, 224, 223, 222, 221 [$M^+ - Cl_2$, –CO (–H)].

Compound **18**: mp 38–40 °C; NMR, see Table I; IR (liquid film) 2930, 1605, 1450, 1270, 1240, 1220, 1185, 1130, 1100, 980,

(14) Gallagher, G., Jr.; Webb, R. L. *Synthesis* **1974**, 122.

(15) Balsamo et al. reported another route to the esters (*EZ*)-**29** but give no experimental or spectroscopic details in their communication.[16]

(16) Balsamo, A.; Crotti, P.; Macchia, B.; Macchia, F.; Passerini, N. *Chim. Ind.* (Milan) **1976**, *58*, 521.

(17) For example, use of the acids analogous to **20** and **29** with the diene **9** or the dimorpholino compond **5** led to no useful cycloadducts under a variety of conditions. Attempts to make the cycloaddition intramolecular via an amide linkage were also unsuccessful.

870, 790 cm^{-1}; High-resolution mass spectrum calcd for $C_{10}H_{10}O_2Cl^{35}_2Cl^{37}_2$ 305.9376, found m/e 305.9379 ($M^+ - C_5H_8$), calcd for $C_{10}H_{10}O_2Cl^{35}_3Cl^{37}$ 303.9405, found m/e 303.9401, calcd for $C_{10}H_{10}O_2Cl^{35}_4$ 301.9435, found m/e 301.9430; mass spectrum, m/e 308, 306, 304, 302 ($M^+ - C_5H_8$), 291, 289, 287, 285 ($M^+ - OCH_2CH{=}CMe_2$), 69 (base, $C_5H_9^+$).

Compound **19** oil; NMR (200 MHz, $CDCl_3$) δ 5.335 (1 H, br t, J = 7.1 Hz), 4.005 (2 H, d, J = 7.1 Hz), 1.729 (3 H, s), 1.646 (3 H, s); IR (liquid film) 2900, 1605, 1440, 1375, 1190, 1090, 950, 840, 780, 750 cm^{-1}; high-resolution mass spectrum calcd for $C_{14}H_{16}OCl^{35}_4$ 339.9955, found m/e 339.9962 ($M^+ - CH_2O$), calcd for $C_{10}H_{10}O_2Cl^{35}_4$ 301.9435, found m/e 301.9472 ($M^+ - C_5H_8$); mass spectrum, m/e 306, 304, 302 ($M^+ - C_5H_8$), 269, 267, ($M^+ - C_5H_8$ - Cl), 70 ($C_5H_{10}^+$), 69 (base, $C_5H_9^+$).

1-Hydroxy-6,7,8,9-tetrachloro-2-oxatricyclo[4.3.0.0^{4,9}]non-7-ene and 5-*exo*-(Hydroxymethyl)-1,2,3,4-tetrachlorobicyclo[2.2.1]hept-2-en-7-one (8). Concentrated sulfuric acid (55 μL) was added dropwise to a solution of the allyloxy adduct **13** (28 mg, 0.09 mmol) in 0.25 mL of dichloromethane at 0 °C. The brown reaction mixture was warmed to 40 °C with stirring for 13 h, cooled, and diluted with dichloromethane. The organic layer was washed with water and saturated sodium bicarbonate solution, dried over sodium sulfate, and evaporated to give 29 mg of a tan solid. This was purified by chromatography on silica gel, using 1:1 diethyl ether/hexane as eluent, followed by recrystallization from hexane/chloroform to give 21 mg of **8** (82%) as white crystals: mp 122–125 °C (lit.[9] mp 124.5 °C); NMR (200 MHz, $CDCl_3$) δ 4.574 (1 H, br d, J = 7.3 Hz), 4.166 (1 H, d, J = 7.3 Hz), 3.272 (1 H, s), 2.658 (1 H, m), 2.190 (2 H, m); IR (50 mg/mL in CH_2Cl_2) 3485, 2875, 1820 (w), 1595, 1210, 1080, 1050–990, 940 cm^{-1}; mass spectrum, m/e 278, 276, 274 (M^+), 243, 241, 239 (base, M^+ - Cl), 219, 218, 217, 216, 215, 214 [M^+ - CO, $-CH_2OH$ (-H)], 197, 195, 193 (M^+ - CO, $-H_2O$, -Cl), 182, 180, 161, 159.

1-Hydroxy-6,7,8,9-tetrachloro-5,5-dimethyl-2-oxatricyclo-[4.3.0.0^{4,9}]non-7-ene and 6-*exo*-(Hydroxymethyl)-1,2,3,4-tetrachloro-5,5-dimethylbicyclo[2.2.1]hept-2-en-7-one (19). Concentrated hydrochloric acid was added dropwise to a solution of the (dimethylallyl)oxy adduct **18** (32 mg, 0.86 mmol) in acetone at 0 °C. The mixture was warmed to 25 °C and stirred for 2 h. The acetone was removed by rotary evaporation and the resulting residue was extracted with diethyl ether. The combined organic layers were washed with water, dried over sodium sulfate, and evaporated to give 33 mg of a brown oil. The oil was chromatographed on silica gel, using 10% diethyl ether/hexane as eluent to give 23 mg (88%) of **19** as a colorless oil: NMR (200 MHz, $CDCl_3$) δ 4.509 (1 H, dd, J = 1.95, 8.8 Hz), 4.270 (1 H, d, J = 8.8 Hz), 3.87 and 3.32 (1 H, br s, hemiketal and keto forms), [2.099 (d, J = 1.9 Hz, hemiketal form), 1.957 (t, J = 5.1 Hz, keto form), 1 H)], [1.352 (s), 0.92 (s), hemiketal form, 1.217 (s), 1.117 (s), keto form, 6 H)]; IR (liquid film) 3600–3050 (br), 2950, 1825, 1600, 1595, 1470, 1395, 1380, 1280, 1190, 1080, 1020, 800, 740 cm^{-1}; high-resolution mass spectrum calcd for $C_{10}H_{10}O_2Cl^{35}_3Cl^{37}$ 303.9405, found m/e 303.9396 (M^+), calcd for $C_{10}H_{10}O_2Cl^{35}_4$ 301.9435, found m/e 301.9455 (M^+); mass spectrum, m/e 306, 304, 302 (M^+), 278, 276, 274 (M^+ - CO), 269, 267 (M^+ - Cl), 247, 245 (base), 243 (M^+ - CO, $-CH_2OH$), 211, 210, 209, 208 [M^+ - CO, $-CH_2O$, -Cl (-H)].

1-*p*-Tolyl-1-chloroethylene (23). A slight modification of the method of Smith was utilized.[12] The ketone **22** (30 g, 0.224 mol) was added dropwise over 1 hour to phosphorus pentachloride (51.2 g, 0.246 mol) at -5 °C under a nitrogen atmosphere. The reaction mixture was warmed to 25 °C whereupon the yellow solid dissolved to give a yellow solution, and this was then heated to 80 °C for 9 h. Phosphorous oxychloride was removed by distillation at reduced pressure and the residue was taken up in diethyl ether, washed with saturated sodium bicarbonate solution, dried over sodium sulfate, evaporated, and distilled through a Vigreux column to give 23.29 g (69%) of **23** as a slightly yellow oil: bp 81–83 °C (10 mm) (lit.[12] bp 81–83 °C (10 mm)); NMR ($CDCl_3$) δ 7.50 (2 H, d, J = 8 Hz), 7.12 (2 H, d, J = 8 Hz), 5.68 (1 H, d, J = 2 Hz), 5.43 (1 H, d, J = 2 Hz), 2.36 (3 H, s); IR (liquid film) 3025, 2910, 1610, 1500, 1220, 1180, 1106, 1010, 865, 810, 750, 708, 615 cm^{-1}.

2-Methyl-3-*p*-tolylbut-3-en-2-ol (24). Magnesium metal (0.799 g, 32.8 mmol) was placed in a flame-dried flask under an atmosphere of nitrogen and enough tetrahydrofuran (THF) to cover the surface of the metal was added. The reaction was initiated by addition of a small amount of dibromoethane and 5.0 g of the vinyl chloride **23** (32.8 mmol) in 8 mL of THF was added dropwise. The solution was refluxed for 1 h after the addition was complete. Then 2.0 mL of acetone (27.2 mmol) was added dropwise and refluxing was continued for 3 h. The reaction mixture was cooled, poured onto saturated ammonium chloride solution, and extracted well with diethyl ether. The combined organic extracts were washed with brine, dried over sodium sulfate, and evaporated to give 7.76 g of a yellow oil which was distilled through a Vigreux column to give 3.52 g (73%) of the alcohol **24** as a colorless oil, bp 60–63 °C (0.55 mm). Further purification could be effected by chromatography on silica gel, using 3:1 diethyl ether/hexane eluent; however, the distilled material was generally of sufficient purity to be carried on to the next step. **24**: NMR (60 MHz, $CDCl_3$) δ 7.15 (4 H, s), 5.39 (1 H, d, J = 2 Hz), 4.93 (1 H, d, J = 2 Hz), 2.35 (3 H, s), 1.65 (1 H, s), 1.40 (6 H, s); IR (liquid film) 3650–3200 (br), 2980, 1630, 1515, 1450, 1380, 1180, 1120, 1080, 960, 910, 825, 770, 730 cm^{-1}.

3-Methyl-2-*p*-tolylbut-2-en-1-ol Acetate (25) and 2-Methyl-3-*p*-tolyl-1,3-butadiene (26). The alcohol **24** (1.47 g, 8.35 mmol) was dissolved in 10 mL glacial acetic acid at 0 °C and 2 drops of concentrated sulfuric acid was added. The reaction mixture was stirred at 10–20 °C for 2.5 h and diluted with 10 mL of water, and the acid was neutralized by addition of solid potassium carbonate. The aqueous solution was extracted with diethyl ether, and the organic phase was dried over sodium sulfate and evaporated to give 1.6 g of a yellow oil. This was subjected to separation by HPLC (Waters Prep 500), using 5% ethyl acetate/hexane as eluent, to afford 1.42 g (78%) of the acetate **25** and 0.158 g (12%) of the butadiene **26**, both as colorless oils.

Acetate **25**: NMR (60 MHz, $CDCl_3$) δ 7.05 (m, 4 H), 4.80 (br s, 2 H), 2.33 (s, 3 H), 1.95 (s, 3 H), 1.89 (s, 3 H), 1.61 (s, 3 H); IR (liquid film) 2930, 1730, 1500, 1435, 1360, 1230, 1010, 940, 810, 720 cm^{-1}.

Diene **26**: NMR (60 MHz, $CDCl_3$) δ 7.1 (4 H, s), 5.21 (1 H, br s), 5.07 (2 H, br s), 4.85 (1 H, br s), 2.3 (3 H, s), 1.93 (3 H, d, J = 1 Hz); IR (liquid film) 2950, 1600, 1515, 1450, 1380, 900, 830 cm^{-1}.

3-Methyl-2-*p*-tolylbut-2-en-1-ol (20). The acetate **25** (6.36 g, 29.1 mmol) was added dropwise to a solution of 12.9 g of potassium carbonate (87.3 mmol) in 23 mL of water, and methanol was added until the reaction mixture became cloudy (~65 mL). This mixture was stirred for 4 h at 25 °C, the methanol was removed by rotary evaporation, and the resulting aqueous solution was extracted well with diethyl ether. The combined organic extracts were washed with brine, dried over sodium sulfate, and evaporated to give 5.3 g of an oil which was distilled to give 5.0 g (98%) of the desired alcohol **20**: bp 90 °C (0.8 mm); NMR (60 MHz, $CDCl_3$) δ 7.08 (4 H, s), 4.33 (2 H, br s), 2.3 (3 H, s), 1.87 (3 H, s), 1.60 (4 H, br s, CH_3 + OH); IR (liquid film) 3700–3100 (br), 2950, 1650, 1510, 1440, 1370, 1290, 1125, 1105, 1035, 990, 810, 780, 730 cm^{-1}.

Reaction of 9 with 20. Powdered potassium hydroxide (107 mg, 1.908 mmol) in 2.2 g of the alcohol **20** was added dropwise at 0 °C to a solution of 187 mg (0.685 mmol) of hexachlorocyclopentadiene (**9**) in 1.98 g of the alcohol **20** under a nitrogen atmosphere. The reaction mixture was stirred at 25 °C for 24 h, poured onto 50 mL of ice water, and extracted with dichloromethane. The dichloromethane extracts were washed with brine, dried over sodium sulfate, and evaporated to give 3.69 g of a yellow oil which contained very large amounts of the alcohol **20**. This was chromatographed on silica gel, using 2% ethyl acetate/hexane as eluent. This afforded the diene **26** (197 mg) as the only new product and recovered starting materials, **9** and **20**.

(*E*)- and (*Z*)-Ethyl 2,3,4′-Trimethylcinnamates ((*EZ*)-29). Ethanol (70 mL) was added dropwise to 1.69 g of sodium (73.9 mmol) under a nitrogen atmosphere and stirred until all of the sodium dissolved. Triethyl α-phosphonopropionate[14] (**28**; 15.99 g, 67.1 mmol) was added and stirring was continued for 30 min. The ketone **22** (9.0 g, 67.1 mmol) was then added dropwise, and the mixture was heated to reflux for 24 h, cooled, poured into water, and extracted with benzene. The benzene extracts were dried over sodium sulfate and evaporated to give a brown oil which was fractionally distilled to give 6.87 g (46%) of a mixture of isomeric olefins (bp 85–90 °C (0.6 mm)). The geometric *E* and

Z isomers were separated by HPLC, using 2% ethyl acetate/hexane as eluent, to give 4.58 g of the less polar *E* ester **29** and 2.29 g of the more polar *Z* ester **29**.[15,16]

(*E*)-**29**: NMR (60 MHz, $CDCl_3$) δ 7.08 (4 H, m), 4.25 (2 H, q, J = 7 Hz), 2.34 (3 H, s), 2.04 (3 H, q, J = 0.9 Hz), 1.76 (3 H, q, J = 0.9 Hz), 1.31 (3 H, t, J = 7 Hz).

(*Z*)-**29**: NMR (60 MHz, $CDCl_3$) δ 7.08 (4 H, m), 3.88 (2 H, q, J = 7 Hz), 2.32 (3 H, s), 1.95 (3 H, br s), 1.93 (3 H, br s) 0.87 (3 H, t, J = 7 Hz).

(*EZ*)-**29**: IR (liquid film) 2940, 1730, 1515, 1450, 1370, 1255, 1140, 1100, 1060, 840 cm^{-1}.

2,3,4′-Trimethylcinnamyl Alcohol (27). The ester (*E*)-**29** (4.25 g, 19.5 mmol) dissolved in 20 mL of diethyl ether was added dropwise to a suspension of lithium aluminum hydride (0.888 g, 23.4 mmol) in 100 mL of diethyl ether at 0 °C. The mixture was stirred at 0 °C for 45 min and then quenched by successive addition of 0.9 mL of water, 0.9 mL of 15% sodium hydroxide solution, and 2.7 mL of water. The aluminum salts were filtered and washed with ether, and the combined ether layers were dried over sodium sulfate and evaporated to give 3.77 g of a yellow oil. Distillation produced 3.02 g (88%) of the alcohol **27** as a colorless oil: bp 125–30 °C (0.4 mm); NMR (60 MHz, $CDCl_3$) δ 7.05 (m, 4 H), 4.31 (br s, 2 H), 2.34 (3 H, s), 2.02 (3 H, br s), 1.69 (3 H, br s), 1.55 (1 H, br s); IR (liquid film) 3700–3125 (br), 2930, 1660, 1520, 1450, 1380, 1110, 1000, 820, 725 cm^{-1}.

Reaction of 9 with 27. Powdered potassium hydroxide (91 mg, 1.61 mmol) dissolved in 1.4 g of the allylic alcohol **27** was added dropwise to a solution of 176 mg (0.65 mmol) of hexachlorocyclopentadiene (**9**) in 1.442 g of the allylic alcohol **27** at 0 °C under a nitrogen atmosphere. The reaction mixture was warmed to 25 °C and stirred for 21 h, poured onto 50 mL of ice water, and extracted with dichloromethane. The combined organic extracts were washed with brine, dried over sodium sulfate, and evaporated to give 3.91 g of a yellow oil which was chromatographed on silica gel, using 3% ethyl acetate/hexane as eluent. This produced only recovered starting material.

Acknowledgment. We thank Professor F. A. L. Anet for helpful discussions. The Bruker WP-200 NMR spectrometer was purchased with funds provided by a major instrument grant from NSF.

Registry No. 8 (keto form), 80516-08-1; 8 (hemiketal form), 80516-09-2; **9**, 77-47-4; **12**, 52144-62-4; **13**, 80516-10-5; **16**, 80516-11-6; **17**, 80516-12-7; **18**, 80516-13-8; **19** (keto form), 80516-14-9; **19** (hemiketal form), 80516-15-0; **20**, 34139-34-9; **22**, 122-00-9; **23**, 42107-37-9; **24**, 80516-16-1; **25**, 80516-17-2; **26**, 80516-18-3; (*E*)-**27**, 34716-99-9; **28**, 3699-66-9; (*E*)-**29**, 61712-12-7; (*Z*)-**29**, 61712-22-9; allyl alcohol, 107-18-6; dimethylallyl alcohol, 556-82-1.

S,N Double Rearrangement. 2.[1] X-ray Crystal Structures of Rearranged Products

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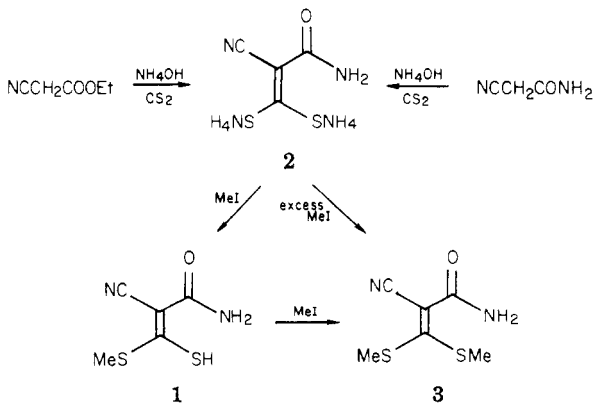
Condensation of 2-cyano-3-mercapto-3-(methylthio)acrylamide (**1**) with benzoic acid in the presence of polyphosphate ester gave 5-carbamoyl-4-(methylthio)-2-phenyl-1,3-oxazine-6-thione (**6**), which, on treatment with boiling ethanol, was easily converted into 5-carbamoyl-4-(methylthio)-2-phenyl-1,3-thiazin-6-one (**9**). Reduction of **9** with $NaBH_4$ gave its 2,3-dihydro derivative **10**. The structures of **6**, **9**, and **10** were determined by single-crystal X-ray diffraction. A reaction mechanism of this novel S,N double rearrangement is briefly discussed.

In the course of the syntheses of 1,3-thiazines and related compounds, we found an interesting condensation reaction which involved a novel rearrangement. Thus, 2-cyano-3-mercapto-3-(methylthio)acrylamide (**1**) reacted with benzoic acid in the presence of polyphosphate ester (PPE)[2] to give 5-carbamoyl-4-(methylthio)-2-phenyl-1,3-thiazin-6-one (**9**).[3] The structures of **9** and its 2,3-dihydro derivative **10** were unequivocally determined by routine single-crystal X-ray analyses. This novel condensation reaction was termed "S,N double rearrangement" and was reported in our preliminary communication.[1] Further investigation led to the isolation of a key intermediate **6**. Its X-ray structural study showed that **6** was a S,N double rearranged product, 5-carbamoyl-4-(methylthio)-2-phenyl-1,3-oxazine-6-thione. We present here more detailed results of this rearrangement and discuss the reaction mechanisms.

Results and Discussion

Structure of 1. Starting material **1** was prepared by the reaction of ethyl cyanoacetate or cyanoacetamide with carbon disulfide in the presence of ammonia, followed by monomethylation using 1 equiv of methyl iodide. In this

Scheme I



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(1) A preliminary account of some of this work has been published: M. Yokoyama, M. Nakamura, T. Imamoto, and K. Yamaguchi, *J. Chem. Soc., Chem. Commun.*, 560 (1981).
(2) W. Pollmann and G. Schramm, *Biochem. Biophys. Acta*, **80**, 1 (1964).

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