(11) (a) B. Lindberg and G. Bergson, *Ark. Kemi*, **23**, 319 (1965); (b) S. H. Smallcombe and M. C. Caserio, *J. Amer. Chem. Soc.*, **93**, 5826 (1971); (c) R. F. Hudson and F. Filippini, *J. Chem. Soc. Chem. Commun.*, 726 (1972); (d) T. C. Morrill, R. J. Opitz, and R. Mozzer, *Tetrahedron Lett.*, 3715 (1973); (e) S. Oae and M. Yoshihara, *Bull. Chem. Soc. Jap.*, **41**, 2082 (1968).

(12) For qualitative evidence for episulfonium ions from β-halo disulfides, see F. Lautenschlaeger and N. V. Schwartz, *J. Org. Chem.*, **34**, 3991 (1969), and N. M. Karimova, M. G. Lin'kova, O. V. Kil'disheva, and I. L. Knunyants, *Khim. Geterotsikl. Soedin.*, (1), 8 (1973) [*Chem. Abstr.*, **78**, 123970 (1973)].

(13) (a) A somewhat similar situation may prevail for $CH_3SSCH_2\cdot$ [*cf.* P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **93**, 846 (1971)]; (b) for a dramatic demonstration of acceptive resonance by divalent sulfur, see C. B. Quinn and J. R. Wiseman, *ibid.*, **95**, 6120 (1973).

(14) J. H. Bowie, S.-O. Lawesson, J. O. Maden, C. Nolde, G. Schroll, and D. H. Williams, *J. Chem. Soc. B*, 946 (1966).

(15) I. Saito and S. Fukui, *J. Vitaminol. (Kyoto)*, **12**, 244 (1966).

(16) E. Block and S. W. Weidman, *J. Amer. Chem. Soc.*, **95**, 5046 (1973).

(17) An extreme example of a stabilized cyclic α-disulfide carbonium ion is the aromatic 1,2-dithiolium ion [*cf.* A. Hordvik, *Quart. Rep. Sulfur Chem.*, **5**, 21 (1970)].

(18) The C–S–S–C dihedral angle in dimethyl disulfide is actually somewhat less than 90° (~85° in the gas phase[19]) and a similar situation may prevail for CH_3SSCH_2Cl and ion **1**. Preliminary kinetic measurements on the rate of hydrolysis of $(CH_3)_3CSSCH_2Cl$, a compound which on steric grounds[19] might be expected to have a dihedral angle closer to 90°, indicate a rate constant less than half as large as that for CH_3SSCH_2Cl. This result, which is in the opposite direction from that expected on the basis of inductive effects, is consistent with the dihedral angle arguments presented above.

(19) H. Bock and G. Wagner, *Angew. Chem., Int. Ed. Engl.*, **11**, 150 (1972).

(20) A. Rieche and C. Bischoff, *Chem. Ber.*, **94**, 2457 (1961); A. Rieche, C. Bischoff, and P. Dietrich, *ibid.*, **94**, 2932 (1961). I thank Dr. José Pazos for bringing these parallels to disulfide chemistry to my attention.

(21) Visiting Professor at Harvard University, 1974. Address correspondence to author at the Department of Chemistry, Harvard University, Cambridge, Mass. 02138.

Department of Chemistry
University of Missouri—St. Louis
St. Louis, Missouri 63121

Eric Block[21]

Received December 12, 1973

The Chlorination of Cyclopentadiene

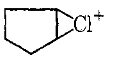
Summary: Chlorination of cyclopentadiene under ionic condition in several solvents produces (in varying amounts) the following dichlorides (yields ~60%): *cis*-3,4-dichlorocyclopentene (**1**), *trans*-3,4-dichlorocyclopentene (**2**), *cis*-3,5-dichlorocyclopentene (**3**), and *trans*-3,5-dichlorocyclopentene (**4**); **1** is formed by cis-1,2 addition of chlorine.

Sir: We wish to report the first example of extensive *cis*-1,2 addition of chlorine to a simple, aliphatic olefinic system.[1] The results in Table I show that chlorination of cyclopentadiene gives *cis*-3,4-dichlorocyclopentene (**1**) under all of the conditions that were examined.

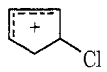
Table I
Chlorination of Cyclopentadiene

Solvent	Percentage of dichlorides 1	2	3	4	Yield, %
CH_2Cl_2	38	35	18	9	52
CCl_4	27	23	39	11	60
C_5H_{12}	13	29	29	28	68

The stereochemistry of 1,2 addition of chlorine to cyclopentadiene stands in marked contrast to cyclopentene. We have established that chlorination of cyclopentene does not give a trace of the cis-1,2 isomer.[2] We account for the difference in the stereochemistry of 1,2 addition between these two olefins on the basis of the bonding between the chlorine and carbon atoms in intermediates **5** and **6**.



5



6

Intermediate **5** (from cyclopentene) gives only trans addition, apparently because bonding between the carbon atoms and chlorine atoms prevents cis attack of the chloride ion. By contrast, intermediate **6** (from cyclopentadiene) has no bonding (or weak, in the case of pentane) between the chlorine atom and adjacent allylic carbon atom, and the chloride ion can attack either cis or trans to the chlorine atom. The results in Table I also suggest that the charge density in intermediate **6** in the least polar solvent pentane is highly dispersed since considerable attack occurs at both ends of the allylic system (ratio of 1,2:1,4 addition equals 1:1.3). In polar dichloromethane the charge density is substantially localized at one allylic carbon atom (ratio of 1,2:1,4 addition equals 1:0.3).

Our results are in sharp disagreement with rather recent studies on the chlorination of cyclopentadiene. One study[3] states that the only product is **4**, and the other investigators claim[4] that 3,5-dichlorocyclopentene (85%) is the principal product (3,4-dichlorocyclopentene, 15%); the stereochemistry was not established.[5]

Reactions were carried out (−15°) at 0.02 mol fraction in diene in the selected solvent (reaction volume ~25 ml) in the presence of O_2. The chlorine was added both as a gas and dissolved in solvent, without any significant differences. Under these conditions cyclohexane was not chlorinated, which confirmed ionic conditions. (Under radical conditions cyclohexane was chlorinated.) Vpc and nmr analyses of reaction mixtures were in close agreement indicating that there was no rearrangement during vpc analysis. Although the yields are not quantitative, the product compositions in Table I seem to be valid since chlorinations at both very low and high completion gave essentially the same mixtures of dichlorides.

Vpc analysis (2.5% SE-30, 18 ft × 0.25 in., 55°, and 100 ml/min) of chlorination mixtures showed four principal peaks with retention times of 9.2, 11.0, 15.4, and 16.4 min. The peaks were assigned to **2**, **4**, **3**, and **1**, respectively. Pure samples of **2** and **4** were isolated from chlorination mixtures by distillation or vpc collection; **1** and **3** were obtained together as a mixture. Samples of **3** and **4** were obtained by independent synthesis from their corresponding dibromides as follows: *cis*- or *trans*-3,5-dibromocyclopentene was allowed to react with excess lithium chloride in DMSO at 15° for 15 min, after which the mixture was added to water and the product extracted into pentane. Structural assignments for **2**, **3**, and **4** are therefore based on independent synthesis (**3** and **4**) and their nmr spectra. The nmr spectra of **2**, **3**, and **4** are strikingly similar to the spectra of the corresponding cyclopentadiene dibromides.[6] The 60-MHz spectral data (CCl_4) for the four dichlorides is summarized as follows. **1:** δ 2.71 (br d, 2, CH_2, $J_{5(5')4}$ = 7.0 Hz), 4.45 (dt, 1, $CH_2C\mathbf{H}Cl$, $J_{45(5')}$ = 7.0, J_{43} = 5.7 Hz), 4.89 (d, 1, $CH{=}CHC\mathbf{H}Cl$, J_{34} = 5.7 Hz), 5.99 (br s, 2, $CH{=}CH$). **2:** 2.52 [br d, 1, *cis*-$C(Cl)C(\mathbf{H})H$, $J_{55'}$ = 18.2 Hz], 3.15 [dd, 1, *trans*-$C(Cl)C(\mathbf{H})H$, $J_{5'5}$ = 18.2, $J_{5'4}$ = 6.0 Hz], 4.48 [d, 1, $CH_2C(\mathbf{H})Cl$, $J_{45'}$ = 6.0 Hz], 4.91 [br s, 1, $CH{=}CHC(\mathbf{H})Cl$], 5.88 (br s, 2, $CH{=}CH$). **3:** 2.30 [dd, 1, *cis*-$C(Cl)C(\mathbf{H})H$, $J_{44'}$ = 15.7, $J_{43(5)}$ = 3.0 Hz], 3.06 [dd, 1, *trans*-$C(Cl)C(\mathbf{H})H$, $J_{4'4}$ = 15.7, $J_{4'3(5)}$ = 7.4 Hz], 4.89 (dd, 2, CHCl, J = 3.0, J = 7.4 Hz), 5.95 (d, 2, $CH{=}CH$, J = 1.0 Hz). **4:** 2.66 (t, 2, CH_2, J = 5.4 Hz), 5.17 (t, 2, CHCl, J = 5.4, J = 1.1 Hz), 6.06 (d, 2, $CH{=}CH$, J = 1.1 Hz).

Assignment of structure **1** to vpc peak no. 4 was made on the basis of the following evidence (a) the ir spectrum of **1** (mixed with **3**) showed no absorptions inconsistent with the proposed structure; (b) when **1** (mixed with 35% **3**) was heated in a sealed tube for 4 days (temp 100°), it largely rearranged to a mixture of **2**, **3**, and **4** (we confirmed that significant net loss of isomers did not occur by including *p*-chlorobromobenzene in the mixture as an internal standard); and (c) the nmr spectrum is consistent with this structure. As stated above, the spectrum showed four regions of absorptions (60 MHz, δ 2.71, 4.45, 4.89, 5.99) with integrated intensities of 2:1:1:2, respectively. Decoupling experiments (Varian XL-100) showed that the multiplet at δ 4.45 collapsed to a doublet when the protons centered at 2.71 were irradiated. Irradiation of the proton centered at δ 4.89 caused the multiplet at 4.45 to collapse to a triplet. The broad doublet at δ 2.71 collapsed to a broad singlet when the proton at 4.45 was irradiated. Unlike the trans-3,4 isomer, **2**, the methylene hydrogens in **1** apparently have the same chemical shift and do not couple with each other.

Acknowledgment. Support for this work was provided by the Research Corporation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Union Oil Co. of California Foundation, Brea, Calif. The authors wish to express appreciation for the use of nmr facilities to the Departments of Chemistry of Southwestern State College, Weatherford, Okla., and the University of Oklahoma, Norman, Okla.

Reference and Notes

(1) Cis-1,2 addition of chlorine has been observed with phenanthrene [P. B. D. de la Mare, N. V. Klassen, and R. Koenigsberger, *J. Chem. Soc.*, 5285 (1961)] and acenaphthalene [S. J. Cristol, F. R. Stermitz, and P. S. Ramey, *J. Amer. Chem. Soc.*, **78**, 4939 (1956)] and has been suspected in the cases of 1-phenylpropene [R. C. Fahey and C. Schubert, *ibid.*, **87**, 5172 (1965)] and stilbene [S. J. Cristol and R. S. Bly, *ibid.*, **82**, 142 (1960)]. In these four olefins the double bond is in conjugation with an aromatic ring.

(2) *cis*-1,2-Dichlorocyclopentane was synthesized according to the procedure that N. Isaacs and D. Kirkpatrick [Tetrahedron Lett., 3869 (1972)] used for the preparation of *cis*-1,2-chlorocyclohexane.

(3) F. Tailly, *Bull. Soc. Chem. Fr.*, 38 (1962).

(4) K. Heinz Buechel, A. Ginsberg, and R. Fischer, *Chem. Ber.*, **99** (2), 421 (1966).

(5) It is conceivable that the structural assignments in the previous studies[3,4] were correct, but that the assignments were made on thermodynamic rather than kinetic products. We have found that the thermodynamic dichloride mixture (formed by heating a dichloride mixture) consists of predominately 3,5-dichlorides. In the previous studies the dichloride products were distilled without regard for rearrangement.

(6) A detailed analysis of the nmr spectra of the dibromides corresponding to dichlorides **2**, **3**, and **4** has recently been published in this journal [G. E. Heasley, V. L. Heasley, S. L. Manatt, H. A. Day, R. V. Hodges, P. A. Kroon, D. A. Redfield, T. L. Rold, and D. E. Williamson, *J. Org. Chem.*, **38**, 4109 (1973)].

Department of Chemistry
Point Loma College
(formerly Pasadena College)
San Diego, California 92106

Victor L. Heasley*
Paul D. Davis
D. Michael Ingle
Kerry D. Rold

Department of Chemistry
Bethany Nazarene College
Bethany, Oklahoma 73008

Gene E. Heasley

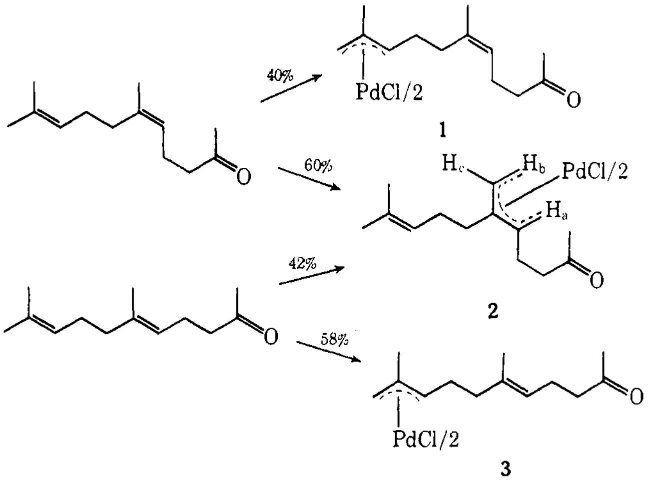
Received October 23, 1973

New Synthetic Reactions. Chemospecificity of Allylic Alkylation

Summary: Selective alkylation of the methyl groups of geranylacetone without protection of the carbonyl group has been aschieved *via* the intermediacy of π-allylpalladium complexes.

Sir: The activation of the α position of carbonyl compounds for formation of carbon-carbon bonds contributes to the importance of the carbonyl group in organic synthesis. The double bond has not generally served such a role.[1] One approach to this problem involves alkylations utilizing π-allylpalladium complexes as intermediates which, in turn, are generated from the olefins.[2] We wish to report that this method allows selective alkylation α to the double bond even in the presence of a carbonyl group.

Treatment of *cis*- or *trans*-geranylacetone with palladium chloride, sodium chloride, cupric chloride, and sodium acetate in acetic acid proceeds regiospecifically to produce the π-allylpalladium chloride dimers **1** and **2** (from cis) and **2** and **3** (from trans) in 70-85% yields.[3,4] The isomers are easily separated by preparative tlc and characterized by their nmr spectra. Isomers **1** and **3** are distinguished from **2** by the presence of the methyl group on the π-allyl unit at δ 2.12 and 2.10, respectively.[5] They are distinguished from each other by the downfield chemical shift of the vinyl methyl group of **1** (δ 1.70) compared to **3** (1.65).[6] It should be noted that the geometry of the double bond of these products completely reflects that of starting material. However, reaction at the central double bond leads to the same π-allylpalladium chloride dimer from either *cis*- or *trans*-geranylacetone.[3] The syn stereochemistry of **2** is assigned on the basis of comparing nmr spectral characteristics (δ_{H_a} 3.40, δ_{H_b} 2.70, and δ_{H_c} 3.63) to related complexes of known stereochemistry.[3,5] Recovered geranylacetone from these preparations shows no loss of double-bond geometry.



The remarkably stability of these complexes is illustrated by the ability to ketalize the carbonyl group without decomposition under normal conditions. On the other hand, such protection was unnecessary for subsequent alkylation. Treatment of either **2** or **3** with the anion of methyl methylsulfonylacetate in the presence of 4 equiv of triphenylphosphine leads to the allylic alkylation products **4** and **5**, respectively, in yields of 24-85% (see Scheme I). To prove the stereochemistry of the newly created double bond, **4** and **5** were converted to the olefins **6** and **7**, a net homologation of the methyl groups of geranylacetone. Lithium iodide in the presence of sodium cyanide effected decarbomethoxylation in 77-78%.[7] Reductive desulfurization was achieved after protecting the carbonyl group in an overall yield of 47-67%.[8] Vpc and nmr characteristics