Stereochemistry and Mechanism of Chlorotelluration of Olefins

Jan-E. Bäckvall, Jan Bergman, and Lars Engman*

Department of Organic Chemistry, Royal Institute of Technology, S-10044 Stockholm, Sweden

Received April 21, 1983

The stereochemistry of the addition of $TeCl_4$ and 2-naphthyltellurium trichloride, respectively, to (*E*)-2-butene, (*Z*)-2-butene, 1-(*E*)-deuterio-1-decene, cyclopentene, cyclohexene, and cyclooctene was studied by means of ^1H nuclear magnetic resonance spectroscopy. The addition of 2-naphthyltellurium trichloride was completely anti stereospecific, whereas $TeCl_4$ usually gave mixtures arising from syn and anti addition. *p*-Benzoquinone was highly effective in promoting syn addition to all olefins investigated when present in a catalytic amount (15–20%). An ionic mechanism involving a telluronium ion intermediate is suggested for the addition of 2-naphthyltellurium trichloride. A more or less concerted, stereospecific syn addition and a competing radical chain reaction are proposed as the major pathways for the addition of $TeCl_4$ to olefins.

Introduction

Tellurium tetrachloride, $TeCl_4$, and alkyl- or aryltellurium trichlorides, $RTeCl_3$, undergo addition reactions with olefins to give the corresponding β-chloroalkyltellurium species **1–3** according to Scheme I.[1-6] When $TeCl_4$ is used as the reagent, 2 mol of olefin may add to give the 2:1 adduct **2**.

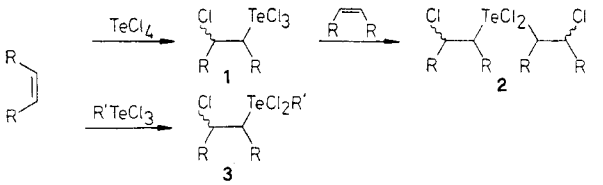
The stereochemistry as well as the regiochemistry of these reactions are virtually unknown.[1,2] Petragnani and co-workers have postulated an anti stereospecific addition in their pioneering work in this area,[3,4] but no experimental evidence has been presented to support this view.

The regiochemistry is generally believed to be Markovnikov. However, the data supporting this statement are based solely on the 2:1 adduct of propene and $TeCl_4$, which has been submitted to a structural investigation.[5]

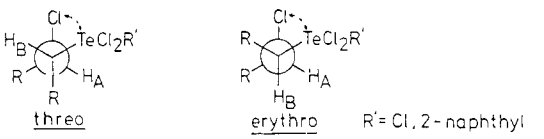
We have recently communicated a method for olefin inversion, involving a postulated syn chlorotelluration–anti dechlorotelluration sequence.[6] The purpose of the present paper is to cast some light on the first part of the sequence, the chlorotelluration reaction. A number of adducts **1** and **3** have been prepared, using olefins, where the stereochemistry of the addition can be determined. We have confined our study to cyclic olefins, symmetrical 1,2-disubstituted olefins, or terminal olefins where the regiochemistry of the addition should cause no further complications.

Determination of Product Stereochemistry. The stereochemical outcome of the chlorotelluration reaction is conveniently determined by using ^1H NMR spectroscopy. The syn and anti adducts usually give distinctly different ^1H NMR signals for the methine protons, which appear in the region 4.5–5.5 ppm. The assignment of the syn and anti addition products is based on the magnitude of the vicinal coupling constants J_{AB} (Scheme II). However, the assumption has to be made that the $TeCl_2R'$ moiety is always gauche to the chlorine atom but anti to the alkyl group R to minimize steric compression. The tellurium atom is electron deficient in the compounds studied, and it is therefore reasonable to expect a weak interaction in solution between tellurium and the electron-rich β-chlorine atom. This phenomenon has previ-

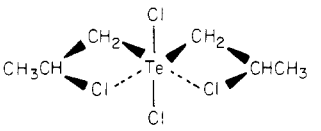
Scheme I



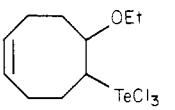
Scheme II



ously been observed in the solid state for the 2:1 adduct of propene and $TeCl_4$ (**4**)[5] and for (8-ethoxy-4-cyclo-



4

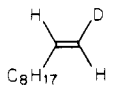


5

octenyl)tellurium trichloride (**5**).[7] Furthermore, similar stabilizing gauche interactions between other metals and a β-heteroatom have been reported.[8]

The conformational restrictions outlined above leave only one favored conformation each for the threo and the erythro isomers, respectively, as shown in Scheme II. According to the Karplus equation,[9] the threo form is expected to have a large vicinal coupling constant, J_{AB}, whereas the erythro form should give a small value for J_{AB}.

The second step of the aforementioned olefin inversion procedure,[6] the Na_2S induced anti elimination to regenerate the olefin, offers a possibility to check the validity of the NMR analyses. This was done in great detail for the adduct of (*E*)-1-deuterio-1-decene (**6**) and $TeCl_4$.[6] The



6

observed values of the coupling constants for the threo and the erythro forms, 10.4 and 4.9 Hz, respectively, were in good agreement with the proposed conformation.

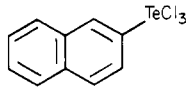
(1) Irgolic, K. J. "The Organic Chemistry of Tellurium"; Gordon and Breach: New York, 1974.
(2) Schmid, G. H.; Garratt, D. G. In "The Chemistry of Doublebonded Functional Groups"; Patai, S., Ed.; Wiley: London, 1977; pp 867, 873.
(3) (a) de Moura Campos, M.; Petragnani, N. *Tetrahedron Lett.* **1959**, (6), 11. (b) Ogawa, M.; Ishioka, R. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 496. (c) Arpe, H. J.; Kuckertz, H. *Angew. Chem. Int. Ed., Engl.* **1971**, *10*, 73.
(4) de Moura Campos, M.; Petragnani, N. *Tetrahedron* **1962**, *18*, 521.
(5) Kobelt, D.; Paulus E. F. *J. Organomet. Chem.* **1971**, *27*, C63.
(6) Bäckvall, J. E.; Engman, L. *Tetrahedron Lett.* **1981**, *22*, 1919.
(7) Bergman, J.; Engman, L. *J. Organomet. Chem.* **1979**, *181*, 335.
(8) (a) Bäckvall, J. E.; Åkermark, B. *J. Organomet. Chem.* **1974**, *78*, 177. (b) Kurosawa, H.; Kitano, R.; Sasaki, T. *J. Chem. Soc., Dalton Trans.* **1978**, 234. (c) Wolfe, S. *Acc. Chem. Res.* **1972**, *5*, 102.
(9) Karplus M. *J. Am. Chem. Soc.* **1963**, *85*, 2870.

0022-3263/83/1948-3918$01.50/0

The described assignment technique has now been applied for derivatives of (*E*)-2-butene, (*Z*)-2-butene, cyclopentene, cyclohexene, and cyclooctene. Except for cyclopentene (vide infra), all derivatives prepared from these olefins show a large coupling constant for the threo (that is, trans in the cyclic series) form (10–12 Hz) and a small coupling constant for the erythro (that is, cis in the cyclic series) form (3–6 Hz).

Results

Addition Reactions of 2-Naphthyltellurium Trichloride. The readily available[10] 2-naphthyltellurium trichloride (7) was chosen as a typical representative of an



7

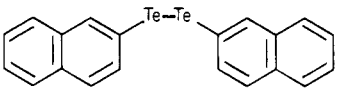
organyltellurium trichloride. Compound **7** was heated in chloroform with a slight excess of (*E*)-2-butene (sealed tube), (*Z*)-2-butene (sealed tube), 1-decene, (*E*)-1-deuterio-1-decene, cyclopentene, and cyclohexene, respectively, to give the crystalline adducts **8–12** (Table I) in good yield. ^{1}H NMR analyses of the crude reaction mixtures in all cases revealed formation of only one stereoisomer. The vicinal coupling constants for the methine protons were in each case determined by selective proton decoupling, and the values are included in Table I together with physical and analytical data.

According to our assignment technique, all products were formed via a stereospecific anti addition to the olefin. Thus, (*Z*)-2-butene gave only an isomer with a large coupling constant (10.2 Hz), which we have assigned as the threo isomer **8b**, and (*E*)-2-butene gave exclusively the erythro isomer **8a**. 1-(*E*)-deuterio-1-decene gave a product, **10**, with a small vicinal coupling constant (4.1 Hz). It was therefore assigned as the erythro isomer **10b**. In the NMR spectrum of the undeuterated isologue **9**, the degenerate AB part of the expected ABX spectrum appears as a doublet (J = 7.8 Hz, an average value of J_{AX} and J_{BX}).[11]

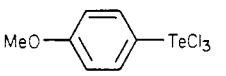
Compounds **8a**, **8b**, **9**, and **10b** were all submitted to a Na_2S treatment, which is known to regenerate the olefin together with 2,2′-dinaphthyl ditelluride (**13**).[10] This reaction most probably occurs anti stereospecifically, in analogy with the Na_2S-induced eliminations of β-chloroalkyltellurium trichlorides.[6] Compound **8a** gave, on treatment with Na_2S, a 94:6 mixture of the *E*:*Z* isomers of 2-butene. Compound **8b** yielded pure (*Z*)-2-butene as determined by GLC analysis. Na_2S reduction of compound **9** regenerated 1-decene in 96% yield. Similar treatment of compound **10b** afforded 1-(*E*)-deuterio-1-decene, free of the *Z* isomer as determined by ^{1}H NMR spectroscopy. The results of the Na_2S reductions in all cases therefore support the assignments made from the values of the vicinal coupling constants.

Compound **11** shows an intermediate value for the vicinal coupling constant (6.2 Hz) and has been assigned the threo configuration **11b**, in analogy with the other results in the series. The conformational analysis does not seem to be applicable for derivatives of cyclopentane (vide infra).

Cyclooctene did not give a product with 2-naphthyltellurium trichloride under the usual reaction conditions. This is probably due to the reversibility of the addition reaction. We also tried to use a different aryltellurium trichloride, (4-methoxyphenyl)tellurium trichloride (**14**),



13



14

in the chlorotelluration, but this resulted in isolation problems for several adducts, which reversed to starting materials on attempted recrystallization.[12]

The stereochemical results of the addition of 2-naphthyltellurium trichloride to various olefins are presented in Table II. A change of solvent in one case from $CHCl_3$ to CCl_4 did not alter the stereochemistry of the reaction.

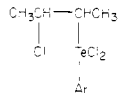
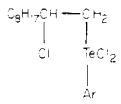
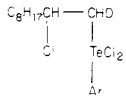
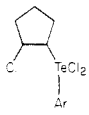
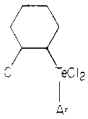
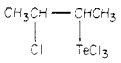
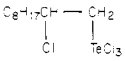
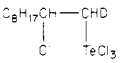
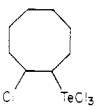
Addition Reactions of Tellurium Tetrachloride. Tellurium tetrachloride, freshly sublimed and finely crushed, was stirred at 0 °C in dry, ethanol-free chloroform or dry acetonitrile with a slight excess of (*E*)-2-butene, (*Z*)-2-butene, 1-decene, (*E*)-1-deuterio-1-decene, cyclopentene, cyclohexene, or cyclooctene, respectively, to give selectively the 1:1 adducts **15–20** (Table I). The stereochemistry of the adducts was determined from the magnitude of the vicinal coupling constants as outlined above, using crude reaction mixtures. Vicinal coupling constants together with physical and analytical data of the purified compounds are given in Table I. The stereochemical results of the chlorotelluration are summarized in Table II. In most of the cases there is a predominance for syn chlorotelluration when $TeCl_4$ is used as the reagent. When the appropriate reaction conditions were chosen, (*E*)-2-butene, (*E*)-1-deuterio-1-decene, cyclopentene, and cyclooctene could be made to undergo a highly stereospecific syn chlorotelluration (>97% syn). The best syn:anti ratio for (*Z*)-2-butene and cyclohexene was 78:22 and 30:70, respectively. The adducts of (*E*)-2-butene and (*Z*)-2-butene were previously prepared as intermediates in an olefin inversion reaction[6] and treated without isolation with Na_2S to regenerate the olefin as a mixture of isomers. The percentage of inverted products nicely parallels the percentage of syn addition obtained in the present study, except for the reaction of (*E*)-2-butene in chloroform (inversion:retention = 80:20 compared with syn:anti = 42:58). This problem of reproducibility led us to investigate the possibility of a competing radical pathway in the addition of $TeCl_4$. Various radical inhibitors that could be expected to be inert toward $TeCl_4$ were therefore added. Neither *p*-dinitrobenzene nor nitromethane had any effect on the stereochemical outcome. Nitrosobenzene was rapidly consumed by $TeCl_4$. Finally, *p*-benzoquinone was tried and found to be highly effective in promoting syn addition to (*E*)-2-butene. The percentage of syn addition could be increased to 88% in the presence of a catalytic amount of benzoquinone (15–20%). All the other experiments were thereafter repeated in the presence of *p*-benzoquinone. The syn:anti ratio was usually considerably increased, as can be seen from Table II. The addition to cyclohexene, which was completely anti stereospecific in the absence of *p*-benzoquinone, now gave 30% of the syn addition product **19a**. The cis and trans isomers **19a** and **19b** obtained from cyclohexene had vicinal coupling constants of 3.3 and 11.3 Hz, respectively, which are typical values for

(10) Bergman, J.; Engman, L. *Tetrahedron* **1980**, *36*, 1275.

(11) Hoffmann, R. A.; Forsén, S.; Gestblom, B. "NMR Basic Principles and Progress"; Diehl, P.; Fluck, E.; Kosfeld, R., Eds.; Springer Verlag: Berlin, 1971; Vol. 5, p 74.

(12) The reversibility of these reactions was demonstrated in a spectacular way during the preparation of the 1:1 adduct of (*Z*)-2-butene and (4-methoxyphenyl)tellurium trichloride. When the reactants had been heated for a while in a sealed tube containing chloroform, almost all of the insoluble aryltellurium trichloride had reacted and gone into solution. At this point the sealed tube started to leak gas due to a small crack in the glass. This resulted in immediate precipitation of (4-methoxyphenyl)tellurium trichloride.

Table I. Chlorotelluration Products. Physical, Analytical and Spectroscopic Data

compd, Ar = 2-naphthyl	stereoisomer	mp, °C	^{1}H NMR data of methine protons: chemical shift, δ	^{1}H NMR data of methine protons: coupling constant, Hz
 8	erythro (8a)[d]	106-108	4.28, 5.12	5.7
	threo (8b)[d]	114-115	4.41, 4.83	10.2
 9	*d*	65-66		
 10	erythro (10a)	63-64	4.13, 4.90	4.1
 11	threo (11b)[d]	84-85	4.48, 4.91	6.2
 12	threo (12b)[d]	149-150 (.it. 136-138)[4]	4.31, 4.71	11.3
 15	erythro (15a)	*a*	4.62, 5.53	4.7
	threo (15b)[d]	106-107	4.86, 4.96	11.2
 16		oil		
	erythro (17a)	oil	4.42, 5.08	4.9
 17	threo (17b)	oil	4.62, 5.08	10.4
 18	erythro (18a)	*b*	5.12, 5.43	6.5
	threo (18b)	*b*	4.80, 5.38	3.3
 19	erythro (19a)	*a*	4.49, 5.68	3.3
	threo (19b)	122-124 (dec) (lit. 112-113)[e]	4.72, 4.91	11.3
 20	erythro (20a)	*c*	4.71, 5.55	4.9

[a] This compound could not be obtained isomerically pure and was characterized only by its ^{1}H NMR spectrum. [b] This compound was an unstable oil that rapidly decomposed on attempted isolation. Chloroform solutions of the compound could be kept for some time before they started to deposit elemental tellurium. [c] This compound could be precipitated as a solid from a chloroform solution by the addition of hexane, but the white material rapidly turned black and gummy after isolation. [d] Satisfactory analytical data (±0.4% for C, H) were obtained for this compound. [e] Reference 3b.

cis- and trans-1,2-disubstituted cyclohexanes.[13] Cyclooctene gave only one isomer, whether the quinone was present or not. The small coupling constant (4.9 Hz) led us to assign it as the syn adduct **20a**.[14]

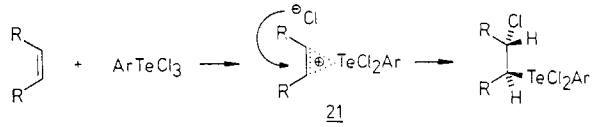
(13) (a) Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed.; Pergamon Press: New York, 1969; pp 280–304. (b) Lemieux, R. V.; Lown, J. W. *Tetrahedron Lett.* **1963**, 1229. (c) Bäckvall J. E.; Oshima, K.; Palermo, R. E.; Sharpless, K. B. *J. Org. Chem.* **1979**, *44*, 1953.

(14) The corresponding oxymercuration adduct, (2-methoxycyclooctyl)mercuric chloride, which is known to be of trans configuration, has a vicinal coupling constant (J_{HH} for -CH(HgCl)CHOMe-) of 8.0 Hz: Waters, W. L. *Tetrahedron Lett.* **1969**, 3769.

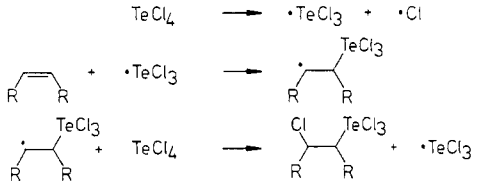
Table II. Stereochemistry of the Chlorotelluration of Olefins

entry	olefin	tellurium reagent (Ar = 2-naphthyl)	solvent	product	syn:anti ratio in the addition
1	(*Z*)-2-butene	$TeCl_4$	$CHCl_3$	15	20:80
2		$TeCl_4$	CH_3CN	15	78:22
3		$TeCl_4$	$CHCl_3$ (benzoquinone)	15	74:26
4	(*E*)-2-butene	$TeCl_4$	$CHCl_3$	15	42:58
5		$TeCl_4$	CH_3CN	15	>97% syn
6		$TeCl_4$	$CHCl_3$ (benzoquinone)	15	88:12
7	(*E*)-1-deuterio-1-decene	$TeCl_4$	$CHCl_3$	17	85:15
8		$TeCl_4$	CH_3CN	17	74:26
9		$TeCl_4$	$CHCl_3$ (benzoquinone)	17	>97% syn
10	Cyclopentene	$TeCl_4$	$CHCl_3$	18	50:50
11		$TeCl_4$	$CHCl_3$ (benzoquinone)	18	>97% syn
12	Cyclohexene	$TeCl_4$	$CHCl_3$	19	>97% anti
13		$TeCl_4$	$CHCl_3$ (benzoquinone)	19	30:70
14	Cyclooctene	$TeCl_4$	$CHCl_3$	20	>97% syn
15		$TeCl_4$	$CHCl_3$ (benzoquinone)	20	>97% syn
16	(*Z*)-2-butene	$ArTeCl_3$	$CHCl_3$	8	>97% anti
17	(*E*)-2-butene	$ArTeCl_3$	$CHCl_3$	8	>97% anti
18		$ArTeCl_3$	$CHCl_3$ (benzoquinone)	8	>97% anti
19	(*E*)-1-deuterio-1-decene	$ArTeCl_3$	$CHCl_3$	10	>97% anti
20		$ArTeCl_3$	CCl_4	10	>97% anti
21	Cyclopentene	$ArTeCl_3$	$CHCl_3$	11	>97% anti
22	Cyclohexene	$ArTeCl_3$	$CHCl_3$	12	>97% anti

Scheme III



Scheme IV



Scheme V

Cyclopentene yielded two isomers in the absence of benzoquinone, the vicinal constants being 3.3 and 6.5 Hz, respectively. In the presence of the inhibitor only the isomer with the larger coupling constant (J = 6.5 Hz) was formed. In analogy with the previous experiments, we have assigned this isomer as (*cis*-2-chlorocyclopentyl)tellurium trichloride (**18a**). It is generally recognized that the information obtained from coupling constants between vicinal ring protons in five-membered rings are of limited value for the assignment of the configuration.[15] Great care must be taken in such assignments since the relative magnitude of J_{cis} and J_{trans} changes with different types of compounds. In many substrates, however, J_{cis} is larger than J_{trans},[16,17] though the opposite is also known.[16] Because of limited NMR data from analogous compounds, our assignment technique fails in this case. The assignment that we have made, however, conforms with the vicinal coupling constant (J_{HH} for –CH(HgCl)CHOMe–) observed in (*trans*-2-methoxycyclopentyl)mercuric chloride, which is 4.1 Hz.[14]

Discussion

The complete anti stereospecificity of the additions of 2-naphthyltellurium trichloride to all olefins studied is consistent with a cyclic telluronium ion intermediate **21** in this reaction (Scheme III). A similar telluronium ion intermediate was originally suggested by Petragnani[4] in the chlorotelluration with $TeCl_4$, in analogy with the mechanism for addition of arylsulphonyl halides to olefins.[18]

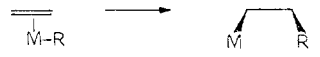
The mechanism of the $TeCl_4$ addition to olefins, on the other hand, is more complex. The results obtained here rule out the mechanism previously suggested,[4] involving a telluronium ion intermediate as the major pathway. Possible side reactions to the favored syn addition would be a radical addition and/or an ionic trans addition via a telluronium ion intermediate. Attempts to detect radicals in the chlorotelluration reaction, using an ESR spin trapping technique, were successful only for (*Z*)-2-octene (in CCl_4), which was used as a model for (*Z*)-2-butene.[19] No signals were obtained, however, from 1-decene, cyclohexene, or (*E*)-2-octene in either CCl_4 or $CHCl_3$. The inhibiting effect of benzoquinone on the side reactions gives further support for the involvement of a radical pathway in the chlorotelluration with $TeCl_4$. A possible radical-chain reaction is outlined in Scheme IV.

A radical addition pathway could explain the poor stereospecificity in many of the additions (Table II). The anti specific addition to cyclohexene is remarkable, but may be a result of a stereospecific radical addition. In fact, many well-documented radical reactions are highly specific, and a strong preference for anti addition was observed for hetero-radical additions to cyclohexenes.[20]

The overwhelming preference for syn addition in all cases where the radical inhibitor is present (except for cyclohexene) suggests a mechanism in which a syn addition of $TeCl_4$ is competing with a radical reaction. Scheme V

(15) Gaudemer, A. In "Stereochemistry. Fundamentals and Methods"; Kagan, H. B., Ed.; Georg Thieme: Stuttgart, 1977; Vol. 1., p 89.
(16) Haubenstock, H.; Mennitt, P. G.; Butler, P. E. *J. Org. Chem.* **1970**, *35*, 3208.
(17) (a) Lipnick, R. L. *J. Am. Chem. Soc.* **1974**, *96*, 2941. (b) Trost, B. M.; Verhoeven, T. R. *Ibid.* **1980**, *102*, 4730.
(18) Kharasch, N.; Buess, C. M. *J. Am. Chem. Soc.* **1949**, *71*, 2724.
(19) Two different spin traps, perdeuterionitrosodurene and *t*-BuNO, were used. In each case a doublet of a triplet was obtained (CCl_4). Perdeuterionitrosodurene: g = 2.0063, a_H = 6.4 G, a_N = 13.3 G; *t*-BuNO: g = 2.0060, a_H = 2.6 G, a_N = 13.9 G. No spectrum could be obtained when the solvent was changed from CCl_4 to $CHCl_3$ or CH_3CN.
(20) Nonhebel, D. C.; Walton, J. C. "Free-radical Chemistry"; Cambridge University Press: London, 1974; p 282.

Scheme VI



R=H, Me, Ar or Cl

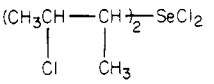
shows a more or less concerted addition of the elements of Cl and $TeCl_3$ across the double bond. Such an addition can formally be regarded as a [2 + 2] cycloaddition. The observation that cyclopentene and (*E*)-2-butene can give >97% syn addition but cyclohexene and (*Z*)-2-butene at most 30% and 78% syn addition, respectively, conforms with the reactivities generally found for cycloadditions. It is well-known that in cycloadditions to olefins, *E* olefins are more reactive than the corresponding *Z* olefins and cyclopentene is considerably more reactive than cyclohexene.[21] The relatively slower syn chlorotelluration expected for cyclohexene and (*Z*)-2-butene would therefore make the competing radical (or anti ionic) pathway more important for these olefins.

The ionic anti stereospecific mechanism postulated for the chlorotelluration with 2-naphthyltellurium trichloride does not seem to be operative to any large extent in the chlorotelluration with $TeCl_4$. Otherwise it would not be possible to obtain the highly stereospecific syn additions for (*E*)-1-deuterio-1-decene, cyclopentene, and cyclooctene on addition of benzoquinone, since benzoquinone should not affect the ionic pathway. A control experiment with (*E*)-2-butene and 2-naphthyltellurium chloride showed that the reaction was unchanged on addition of benzoquinone (Table II, entry 18).

When the solvent was changed from chloroform to acetonitrile, a high preference for syn addition of $TeCl_4$ was observed for (*E*)- and (*Z*)-2-butene, even without a radical inhibitor.[22] It thus appears that the radical pathway is strongly disfavored when this solvent is used.

A stereospecific syn addition to a double bond is of synthetic interest since it constitutes an exception to the anti addition generally observed.[23] Syn additions have been observed for oxymercurations and DBr additions to strained olefins.[24,25] The hydroboration reaction is known to proceed via a syn four-center addition to the double bond.[26] Furthermore, transition-metal-promoted nucleophilic additions to olefins sometimes occur syn.[27] In these reactions a coordinated nucleophile, usually a hydride or an alkyl group, and the metal add syn across the double bond (Scheme VI). Analogous chlorometalations (Scheme VI, R = Cl) have also been suggested to occur syn.[28,29] For example, syn chloropalladation of double bonds may occur under certain conditions,[28] and a syn chlorometalation with a consecutive reductive elimination was suggested[29] to account for the observed syn dichlorination of olefins by $MoCl_5$[30] and CrO_2Cl_2.[29] However, no direct demonstration of these chlorometalations has been provided so far, and to the best of our knowledge our work constitutes the first established example of a syn chlorometalation of an olefin. A related syn chlorotelluration of phenylacetylenes has been reported.[31]

The addition of $SeCl_4$ to olefins yields 2:1 adducts **22**.[32,33]



22

Interestingly, the mechanism of this addition appears to differ from that observed with $TeCl_4$. From the NMR data of the bis adducts **22** and (*E*)- and (*Z*)-2-butene, it was concluded that the chloroselenation had occurred anti.[33]

Experimental Section

Melting points were uncorrected. NMR spectra were obtained with a Bruker WP 200 instrument at 200 MHz. They were recorded in $CDCl_3$ solutions containing Me_4Si as internal standard and are reported in δ units. All olefins used were commercially available except 1-(*E*)-deuterio-1-decene, which was prepared by hydroalumination[34] of 1-decyne followed by D_2O quenching.[35] $TeCl_4$ was sublimed immediately before use (200 °C (0.1 mmHg)) and finely crushed with a glass rod. The chloroform was repeatedly washed with water to remove any trace of EtOH and dried over $CaCl_2$. The acetonitrile was predried over $CaCl_2$, distilled, and stored over 4-Å molecular sieves. 2-Naphthyltellurium trichloride was synthesized according to a literature procedure.[10] *p*-Benzoquinone was freshly sublimed before use.

Synthesis of β-Chloroalkyl-2-naphthyltellurium Dichlorides (8–12). General Procedure. 2-Naphthyltellurium trichloride (0.83 mmol) was heated at reflux with the appropriate olefin (1.2 mmol) in dry, ethanol-free chloroform (15 mL) until the organotellurium compound had dissolved (0.5–1 h). Filtration from a small amount of elemental tellurium and evaporation gave an oil or a semisolid that was recrystallized from a large amount of light petroleum, bp 40–60 °C, to give the analytically pure sample (see Table I). The reactions with (*Z*)- and (*E*)-2-butene were carried out in a sealed tube at 80 °C as described above. Yields of all compounds and complementary ^1H NMR data (methine protons are reported in Table I) are given in the following: **8a**, yield 95%; ^1H NMR 1.77 (d, 3 H), 1.84 (d, 3 H), 7.60–7.65 (several peaks, 2 H), 7.88–7.95 (several peaks, 2 H), 8.00 (d, 1 H, J = 8.7 Hz), 8.22 (dd, 1 H, J = 1.9 Hz), 8.76 (d, 1 H, J = 1.5 Hz).

8b: yield 95%; ^1H NMR 1.68 (d, 3 H), 1.71 (d, 3 H), 7.57–7.68 (several peaks 2 H), 7.88–7.97 (several peaks, 2 H), 8.00 (d, 1 H, J = 8.8 Hz), 8.29 (dd, 1 H, J = 1.8 Hz and 8.9 Hz), 8.83 (d, 1 H, J = 1.3 Hz).

9: yield 76%; ^1H NMR 0.88 (t, 3 H), 1.28–1.60 (several peaks, 12 H), 1.92 (m, 2 H), 4.15 (d, 2 H, J = 7.8 Hz), 4.92 (m, 1 H), 7.60–7.65 (several peaks, 2 H), 7.89–7.98 (several peaks, 2 H), 8.00 (d, 1 H, J = 9.3 Hz), 8.16 (dd, 1 H, J = 1.7 Hz and 9.0 Hz), 8.69 (s, 1 H).

10: yield 71%; ^1H NMR 0.88 (t, 3 H), 1.19–1.56 (several peaks, 12 H), 1.92 (m, 2 H), 4.13 (d, 1 H, J = 4.1 Hz), 4.90 (m, 1 H), 7.60–7.67 (several peaks, 2 H), 7.89–7.97 (several peaks, 2 H), 8.00 (d, 1 H, J = 9.2 Hz), 8.16 (dd, 1 H, J = 1.8 Hz and 8.8 Hz), 8.69 (d, 1 H, J = 1.4 Hz).

11b: yield 98%; ^1H NMR 1.85–2.05 (several peaks, 3 H), 2.25–2.42 (several peaks, 2 H), 2.52 (m, 1 H), 7.58–7.67 (several peaks, 2 H), 7.88–7.97 (several peaks, 2 H), 7.99 (d, 1 H, J = 8.9 Hz), 8.24 (dd, 1 H, J = 1.8 Hz and 8.8 Hz), 8.77 (s, 1 H).

(21) (a) Huisgen, R. *Angew. Chem.* **1963**, *75*, 742. (b) Sauer, J.; Land, P.; Wiest, H. *Z. Naturforsch.* **1962**, *176*, 206. (c) Awasthy, A. K.; Rocek, J. *J. Am. Chem. Soc.* **1969**, *91*, 991. (d) Bailey, A. S.; White, J. E. *J. Chem. Soc. B* **1966**, 819. (e) Sharpless, K. B.; Townsend, J. M.; Williams, D. R. *J. Am. Chem. Soc.* **1972**, *94*, 295.

(22) Attempts to run the $TeCl_4$ reactions with the cyclic olefins in acetonitrile resulted in complicated reaction mixtures where the stereochemistry could not be determined with any accuracy.

(23) Sonnet, P. E. *Tetrahedron* **1980**, *36*, 557.

(24) Traylor, T. G. *Acc. Chem. Res.* **1969**, *2*, 152.

(25) Dewar, M. J. S.; Fahey, R. C. *Angew. Chem.* **1964**, *76*, 320.

(26) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1961**, *83*, 2544.

(27) Bäckvall, J. E. In "Reaction of Coordinated Ligands"; Braterman, P. E., Ed.; Plenum Press: London; in press.

(28) (a) Henry, P. M. *Acc. Chem. Res.* **1973**, *6*, 16; *J. Org. Chem.* **1972**, *37*, 2443. (b) Lucas, J.; Van Leeuwen, P. W. N. M.; Volger, H. C.; Kouwenhoven, A. P. *J. Organomet. Chem.* **1973**, *47*, 153.

(29) Sharpless, K. B.; Teranishi, A. Y.; Bäckvall, J. E. *J. Am. Chem. Soc.* **1977**, *99*, 3120.

(30) (a) Uemura, S.; Onoe, A.; Okano, M. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 3121. (b) San Filippo, J.; Sowinski, A. F.; Romano, L. J. *J. Am. Chem. Soc.* **1975**, *97*, 1599.

(31) Uemura, S.; Miyoshi, H.; Okano, M. *Chem. Lett.* **1979**, 1357.

(32) Riley, R. F.; Flato, J.; Bengels, D. *J. Org. Chem.* **1962**, *27*, 2651.

(33) Garratt, D. G.; Ujjainwalla, M.; Schmid, G. H. *J. Org. Chem.* **1980**, *45*, 1206.

(34) Wilke, G.; Müller, H. *Justus Liebigs Ann. Chem.* **1958**, *618*, 267.

(35) Patrick, D. W.; Truesdale, L. K.; Biller, S. A.; Sharpless, K. B. *J. Org. Chem.* **1978**, *43*, 2628.

12b: yield 95%; ^{1}H NMR 1.31-1.43 (several peaks, 2 H), 1.74-2.00 (several peaks, 5 H), 2.48 (m, 1 H), 7.56-7.67 (several peaks, 2 H), 7.88-8.00 (several peaks, 2 H), 7.99 (d, 1 H, J = 9.0 Hz), 8.31 (dd, 1 H, J = 1.8 Hz and 8.8 Hz), 8.84 (d, 1 H, J = 1.1 Hz).

Na_2S Reduction of Compounds 8a, 8b, 9, and 10a. Compounds **8a** and **8b** were treated with $Na_2S \cdot 9\ H_2O$ (20% aqueous) in an evacuated flask equipped with a septum and an addition funnel. The gaseous products were analyzed by GLC and compared with authentic samples.

Compound **9** (0.50 g, 1.0 mmol) was shaked thoroughly with ethyl ether (50 mL) and $Na_2S \cdot 9\ H_2O$ (20% aqueous, 50 mL). The organic phase was separated, dried ($CaCl_2$), and evaporated to give 0.38 g of a 1:1 mixture of 1-decene and 2,2′-dinaphthyl ditelluride: mp 117-118 °C (EtOH) [lit. 120-122 °C];[36] yield 96%.

Reduction of the deuterated analogue **10a** similarly gave only 1-(*E*)-deuterio-1-decene.

Synthesis of β-Chloroalkyltellurium Trichlorides (15-20). Typical Procedure. Freshly sublimed $TeCl_4$ (1.67 g, 6.2 mmol) and (*Z*)-2-butene (0.36 g, 6.4 mmol) were stirred in an ice-bath for 3 h in dry, ethanol-free chloroform (20 mL) when almost all the $TeCl_4$ had disappeared. Filtration and evaporation yielded 1.35 g of product (67%) as a mixture of isomers **15a** and **15b** (Table II). Recrystallization from acetonitrile afforded the pure threo isomer **15b** as a white crystalline material (Table I).

(*E*)-2-Butene required 3 h at 0 °C and stirring overnight at ambient temperature to give a 94% yield of isomers **15a/15b**. The cyclic and the terminal olefins reacted with $TeCl_4$ within 3 h at 0 °C to give the following yields of addition compounds: cyclopentene (98%), cyclohexene (99%), cyclooctene (83%), 1-decene (98%), and (*E*)-1-deuterio-1-decene (96%). The relative yields of isomers are shown in Table II and physical and analytical data are collected in Table I.

(36) Petragnani, N.; de Moura Campos, M. *Tetrahedron* **1965**, *21*, 13.

The experiments using *p*-benzoquinone were carried out as described in the typical procedure, but in the presence of 15-20 mol % of the quinone. Longer reaction times were frequently required and the reactions were not disrupted until all or most of the $TeCl_4$ had disappeared.

(*E*)-2-Butene again required stirring at ambient temperature overnight. This was also the case with cyclohexene.

Complementary ^{1}H NMR data for compounds **15-20** are given in the following (methine protons are reported in Table I): **15a**, 1.70 (d, 3 H), 2.30 (d, 3 H). **15b**, 1.76 (d, 3 H), 2.22 (d, 3 H). **16**, 0.89 (t, 3 H), 1.26-1.58 (several peaks, 12 H), 1.92 (m, 2 H), 4.42 (dd, 1 H, J = 11.1 and 4.9 Hz), 4.62 (t, 1 H, J = 11.1 Hz), 5.08 (m, 1 H). **17a** and **17b**, 0.89 (t, 3 H), 1.27-1.58 (several peaks, 12 H), 1.92 (m, 2 H). **18a** 1.90 (m, 1 H), 2.20-2.35 (several peaks, 3 H), 2.61 (m, 1 H), 3.55 (m, 1 H). **18b** 2.00-2.35 (several peaks, 4 H), 2.96 (m, 2 H). **19a** Could not be accurately determined. **19b** 1.43-1.68 (several peaks, 2 H), 1.79-2.00 (several peaks, 2 H), 2.09-2.29 (several peaks, 2 H), 2.51 (m, 1 H), 2.70 (m, 1 H). **20a** 1.45-1.88 (several peaks, 7 H), 2.16-2.40 (several peaks, 4 H), 3.32 (m, 1 H).

Acknowledgment. We thank Dr. Sakae Uemura, Institute for Chemical Research, Kyoto University, Uji, Kyoto, Japan, and Dr. Takashi Kawamura, Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan, for running the ESR experiments. Financial support by the Swedish Natural Science Research Council is gratefully acknowledged.

Registry No. **6**, 39106-47-3; **7**, 71578-23-9; **8a**, 87099-35-2; **8b**, 87099-36-3; **9**, 87070-60-8; **10a**, 87070-61-9; **11b**, 87070-62-0; **12b**, 87070-63-1; **15a**, 87099-37-4; **15b**, 87099-38-5; **17a**, 87099-39-6; **17b**, 87144-13-6; **18a**, 87070-64-2; **18b**, 87099-40-9; **19a**, 87099-41-0; **19b**, 87099-42-1; **20a**, 87070-65-3; (*Z*)-2-butene, 590-18-1; (*E*)-2-butene, 624-64-6; cyclopentene, 142-29-0; cyclohexene, 110-83-8; cyclooctene, 931-88-4; $TeCl_4$, 10026-07-0.

Computer-Assisted Mechanistic Evaluation of Organic Reactions. 7. Six-Electron Cycloadditions

Julia Schmidt Burnier and William L. Jorgensen*

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

Received April 4, 1983

An interactive computer program, CAMEO, is being developed to predict the products of organic reactions through the use of mechanistic reasoning. The program has been expanded to encompass six-electron cycloadditions, including reactions of 1,3-dipoles, as the first part of a general module for pericyclic chemistry. A review of the reaction components and their regiochemistry in six-electron cycloadditions is first presented. Next, the development and implementation of algorithms used to predict the likelihood and regio- and stereoselectivity of six-electron cycloadditions are described. The analyses are based on the frontier molecular orbital method. Consequently, it was necessary to devise efficient algorithms for predicting the energies and relative coefficients of frontier molecular orbitals. General empirical relationships were developed on the basis of experimental data and the results of quantum mechanical calculations. Sample sequences are provided that illustrate typical predictions made by the program.

I. Introduction

CAMEO is a computer program designed to predict the products of organic reactions given starting materials and conditions.[1-5] Two key features of the program are that its predictions are made via the simulation of reaction mechanisms and that it is interactive with the input and output of structures occurring at a graphics terminal. Following the input of reactants and conditions, the program enters a perception phase in which important structural features such as functional groups, rings, stereochemistry, and reactive sites are recognized. This in-

(1) T. D. Salatin and W. L. Jorgensen, *J. Org. Chem.*, **45**, 2043 (1980).
(2) T. D. Salatin, D. McLaughlin, and W. L. Jorgensen, *J. Org. Chem.*, **46**, 5284 (1981).
(3) C. E. Peishoff and W. L. Jorgensen, *J. Org. Chem.*, **48**, 1970 (1983).
(4) D. McLaughlin and W. L. Jorgensen, in preparation.
(5) B. L. Roos-Kozel, Ph.D. Thesis, Purdue University, 1981.

0022-3263/83/1948-3923$01.50/0