STERIC CONTROL OF REGIOCHEMISTRY IN THE REACTIONS OF METHYL SUBSTITUTED PENTADIENYL CATIONS WITH ISOBUTENE

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Abstract: The dienylic chlorides 1-5 react with isobutene in the presence of zinc chloride/ether in dichloromethane to give the acyclic adducts 6-10 in 64-91% yield. The orientation effects are in contrast to the predictions of perturbational molecular orbital theory and can be explained on the basis of steric effects.

The odd-numbered alternating π-system, which is incorporated in dienyl cations and anions has attracted the interest of synthetic and theoretical chemists [1]. Various studies on the site of electrophilic attack at pentadienyl anions have been published [2].

Scheme 1[2b]

The most comprehensive report has shown that acyclic potassium dienides give the corresponding 1,3-dienes upon hydrolysis while potassium cycloheptadienide and cyclooctadienide give 1,4-dienes exclusively [2b]. Methylation with methyl iodide also occurs preferentially at the terminal position of the acyclic dienides and at the central position of the cyclic dienides.

The structure of dienylic cations has been studied by NMR spectroscopy in superacid solution [1a]. Their reactivity towards nucleophiles has been derived from the investigation of acid catalysed rearrangements of dienylic alcohols [3,4a] and from the results of solvolysis reactions [4].

Miginiac reported that treatment of 5-chloro-1,3-pentadiene with silver acetate in ether or with aqueous bicarbonate solution yields 1,3-diene derivatives predominantly (Scheme 2) [4a]. Under the same conditions, conjugated dienes were formed exclusively from various hexadienyl cation precursors, i.e., attack at the 3-position of the pentadienyl fragment does not occur. Similar data on solvolyses of chlorohexadienes have been reported by Nazarov [4c].

Scheme 2[4a]

| AgCH$_3$CO$_2$ / Et$_2$O | 82 | 18 | | 65 | 0 | 35 |
| NaHCO$_3$ / H$_2$O | 85 | 15 | | 25 | 0 | 75 |

In contrast to noncoordinated dienylic cations, the corresponding transition metal complexes have also been studied with respect to their reactivity towards carbon nucleophiles. Whereas tricarbonyldienyliron salts react exclusively at the dienyl termini [5a,b], the n' complexes with Pd, Mo and W are also attacked at the central position [5c].

In this paper we report the formation of acyclic adducts of isobutene with various methyl substituted pentadienyl cations. Since the primarily generated adducts may undergo successive cyclisation reactions in analogy to the corresponding allyl cation reactions [6], the position of the initial attack determines which types of carbocycles may be accessible via cycloaddition of dienyl cations with alkenes (Scheme 3).

Scheme 3
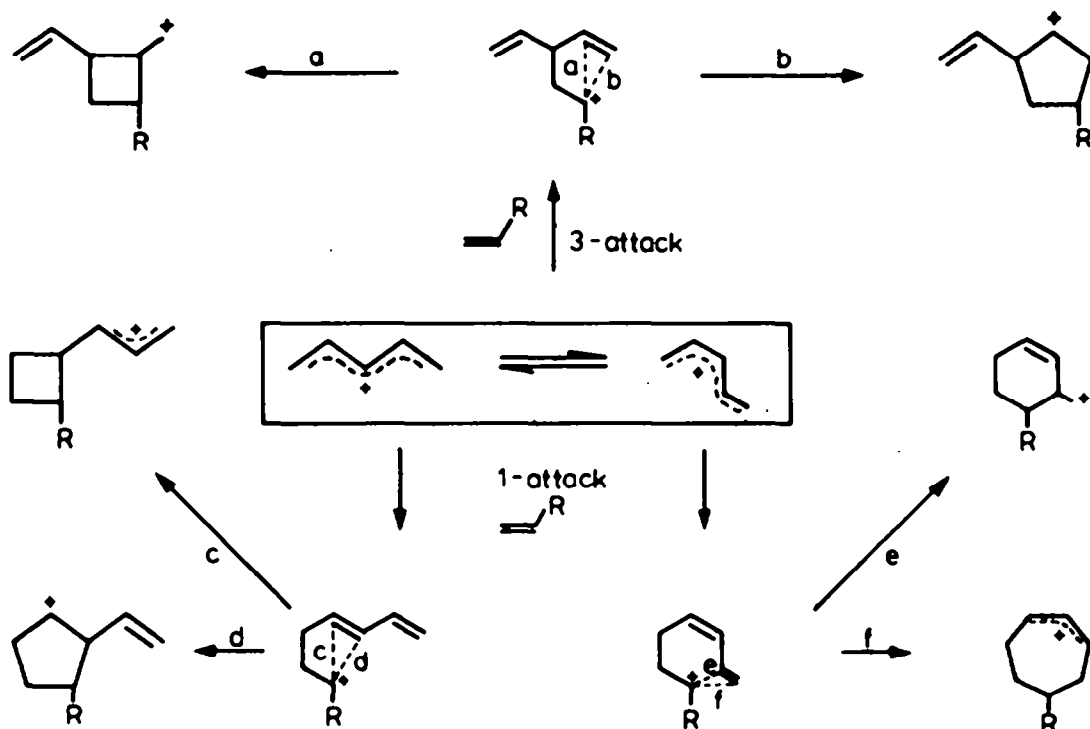
Precursors. Dienylic cations can be generated from the dienyl chlorides 1-5, which have usually been synthesized from 3-hydroxy-1,4-dienes or 5-hydroxy-1,3-dienes. The conversions of the
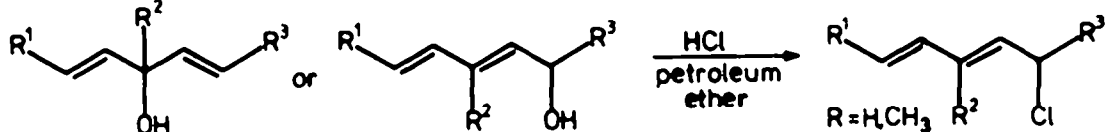
unsaturated alcohols into the corresponding chlorodienes usually proceed in better yield than described in the literature [4a], when solutions of the alcohols in petroleum ether are shaken with 12N aqueous hydrochloric acid.

Table 1. ^{13}C NMR Chemical Shifts of the Chlorodienes 1 - 5

$$R^1 \overset{2}{\underset{1}{\diagup}} \overset{3}{\diagup} \overset{5}{\underset{R^2 \ R^3}{\diagup}} Cl$$

	R¹	R²	R³	C-1	C-2	C-3	C-4	C-5	R¹	R²	R³
1	H	H	H	119.12	135.50	134.72	128.71	44.80	-	-	-
(E)-2	H	CH₃	H	114.59	140.10	139.12	126.53	40.64	-	11.59	-
(Z)-2	H	CH₃	H	116.93	132.05	137.82	124.72	39.66	-	19.77	-
(E),(E)-3	CH₃	H	H	130.15	131.83	134.74	125.55	45.49	18.16	-	-
(E),(E)-4	CH₃	H	CH₃	130.17	131.83ᵃ	131.39ᵃ	131.53ᵃ	58.41	18.17	-	25.31
5	R¹,R³=CH₂-CH₂,R²=H			131.74	126.38	124.31	136.35	60.12	25.57	-	33.73

ᵃ Assignments uncertain

Results. When the dienyl chlorides 1–5 were treated with 1-6 equivalents of isobutene in the presence of zinc chloride/ether [7] at -78°C, the 1:1 products 6-10 were produced in 64-91% yield (Table 2). The addition products are characterized by ¹H NMR singlets at δ 1.56 - 1.61, which indicate the presence of C(CH₃)₂Cl fragments and exclude the formation of cyclized products. The ¹³C NMR data (Table 3) support the structural assignments.

Table 2. Zinc Chloride Catalyzed Additions of the Dienylic Chlorides 1 - 5 with Isobutene in CH₂Cl₂ at -78°C.

Dienyl Chloride	[Isobutene] (Dienyl Chloride)	Time (h)	Products		Yield (%)
1	1.2	76	6		65
2 a)	6.1	144	7 b)		64
3 c)	4.0	17	8a	8b	72 (~10:1)
4	4.0	5	9a	9b	79 (~30:1)
5 d)	1.9	2	10a	10b	91 (~1:3)

a) (E):(Z) = 2.5 : 1; b) (E):(Z) = 4 : 1; c) With 20% of the allylic isomer 5-chloro-1,3-hexadiene; d) Contaminated by 20% of 6-chloro-1,3-cycloheptadiene, which is inert under the reaction conditions.

Table 3. ^{13}C NMR Chemical Shifts of the Addition Products 6 - 10

	R^1	R^2	R^8	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	R
6	H	H	H	115.12	137.00	131.35	133.93	28.30	45.26	70.32	32.40	-
(E)-7	H	CH$_3$	H	110.79	141.30	134.51	131.69	24.18	45.47	70.47	32.40	11.62
(Z)-7	H	CH$_3$	H	113.76	133.38	132.78	129.68	23.30	45.90	**	**	19.75
8a	CH$_3$	H	H	127.25	131.46	130.77*	130.58*	28.32	45.56	70.52	32.41	18.00
8b	H	H	CH$_3$	115.16	137.18	129.28	141.41	**	52.61	**	33.70	22.94
											34.33	
9a	CH$_3$	H	CH$_3$	127.25	131.57	128.67	138.16	34.39	52.78	71.30	32.38	18.02
											33.76	23.20
10a	R^1,R^3-CH$_2$-CH$_2$	R^2-H		133.99	124.80*	123.58*	138.90	37.59	52.12	**	32.73*	28.79
											33.49*	**
9b	CH$_3$	H	CH$_3$	124.19	135.21	43.17	135.21	124.19	50.88	**	33.15	**
10b	R^1,R^3-CH$_2$-CH$_2$	R^2-H		129.20	135.48	34.95	135.48	129.20	52.99	70.80	33.00	25.97

** Signal covered.   * Assignments uncertain.

Table 2 shows that the reaction times roughly decrease with increasing alkyl substitution of the dienyl fragment reflecting the increasing rates of ionization. Two types of sequential reactions of the products 6-10 have to be considered: (i) ionization of the tertiary chlorides and electrophilic attack at additional isobutene molecules (—> isobutene polymerization) and (ii) electrophilic attack of the dienyl cations at the π system of 6-10. Since an excess of isobutene, which favours reaction (i) and represses reaction (ii), was found to improve the yields of 1:1 products, we conclude that side reaction (i) does not play a role under these conditions. This result is expected on the basis of the high solvolysis rates of dienyl derivatives [4b] and our previous studies on the relationship between S$_N$1 reactivity and relative alkylating ability of alkyl halides [8].

Discussion. In analogy to the corresponding reactions of allylic chlorides [6], compounds 1-5 can be assumed to react via the dienylic cations 1$^+$-5$^+$. Their electronic structure has been investi-

Table 4. MINDO Calculations of Some Dienylic Cations [a,b]

Cation	LUMO coefficients				Formal charges			ΔH_f°
	c$_1$	c$_3$	c$_5$	c$_3$/c$_1$	C-1	C-3	C-5	(kcal/mol)
1$^+$	-0.517	+0.680	-0.517	1.32	0.243	0.326	0.243	219.7
					(0.257)	(0.397)	(0.257)	(215.1)
2$^+$	-0.496	+0.692	-0.496	1.40	0.227	0.307	0.228	215.0
					(0.229)	(0.393)	(0.222)	(210.4)
3$^+$	-0.546	+0.664	-0.488	1.21	0.214	0.312	0.225	207.3
					(0.324)	(0.376)	(0.219)	(196.4)
4$^+$	-0.517	+0.653	-0.517	1.26	0.196	0.300	0.196	195.1
5$^+$	-0.524	+0.653	-0.513	1.25	0.188	0.314	0.181	206.7

[a] The π-framework and the attached atoms have been kept planar in 1$^+$-4$^+$. All other geometric parameters have been optimised.   [b] MINDO/3-values from ref. 1c in parentheses.

gated using the semiempirical MNDO method [9]. Table 4 shows that in all cases the absolute value of the LUMO coefficient as well as the formal positive charge attains a maximum at C-3. Methyl groups increase the absolute value of the LUMO coefficient at the substituted carbon and decrease this value at remote positions, analogous to the situation in other π delocalised carbenium ions [10].

According to PMO theory, uncharged nucleophiles are expected to attack at the position with the largest LUMO coefficient [11], i.e., at C-3. Table 4 shows, however, that products derived from C-3 attack were not at all observed with cations 1^+-3^+. The formation of 9a,b and 10a,b indicates, however, that cations 4^+ and 5^+ can react at the terminal and the central position though PMO theory predicts a reduced preference of C-3 attack in these cases (reduced c_s/c_1 (LUMO) ratio).

The unsymmetrically substituted cation 3^+ yields more of the adduct 8a than of the isomeric 8b. While a sequence C-3 > C-1 > C-5 attack is predicted by PMO theory, exactly the reverse order is experimentally found.

We, therefore, conclude that the electronic effects caused by methyl groups are overcompensated by steric effects. As previously reported for allyl cation additions [6d], the regiochemistry of the addition reactions of dienylic cations with isobutene can be rationalized on the basis of steric effects.

EXPERIMENTAL

^{1}H NMR spectra: JNM-C-60-HL (JEOL), EM-390 and XL-200 (Varian). ^{13}C NMR spectra: JNM-PS-100 (JEOL) and XL-200 (Varian). TMS as internal standard. Mass spectra: CH 4 B MAT (Varian), 311 A MAT (Varian), and 70-250 (VG); only the most intensive mass peaks are listed.

Dienyl Chlorides 1-4 were prepared from 1,4-pentadien-3-ol [4a], 3-methyl-1,4-pentadien-3-ol [12], 2,4-hexadien-1-ol [13], and 3,5-heptadien-2-ol [14] and aqueous HCl according to a modified literature procedure [4a]. The preparation of 5 is described in the following paper.

5-Chloro-1,3(E)-pentadiene 1 (General procedure). 55 mL of 12 M aqueous HCl were added dropwise to a precooled (0°C) solution of 27.2 g (323 mmol) 1,4-pentadien-3-ol in 330 mL of petroleum ether. After stirring the suspension at 0°C for 17 h the phases were separated. The organic layer was dried with Na₂SO₄ and distilled to give 24.0 g (72%) of 5-chloro-1,3(E)-pentadiene 1 with bp 36 - 40°C/50 mbar (lit. [4a] 57%, bp 33°C/39 mbar).

5-Chloro-1,3(E)-pentadiene 1 and Isobutene (General Procedure). A solution of 1 (2.05 g, 20.0 mmol) in 10 mL of CH₂Cl₂ was added dropwise to a precooled (-78°C) solution of isobutene (1.40 g, 25.0 mmol) and ZnCl₂ (2.02 g)/ether (1.68 mL) [15] in 38 mL of CH₂Cl₂. The reaction mixture was kept at -78°C for 76 h and washed with 40 mL of 25% aqueous NH₄Cl solution. The organic layer was dried with CaCl₂ and distilled to give 0.25 g of unreacted 1 and 1.80 g (65% based on reacted 1) of 7-chloro-7-methyl-1,3-octadiene 6. - bp 33 - 35°C (bath)/0.5 mbar. - ^{1}H NMR (CCl₄, 60 MHz): δ 1.58 (s, 6 H, C(CH₃)₂Cl), 1.63 - 2.03 (m, 2 H, 6-H), 2.03 - 2.66 (m, 2 H, 5-H), 4.73 - 5.36 (m, 2 H, -CH₂), 5.36 - 6.63 (m, 3 H, 2,3,4-H). - Mass spectrum (80 eV): m/z - 160, 158 (25%, 72%, M⁺), 122 (80), 107 (90), 91 (78), 79 (100), 67 (58). - Anal. Calcd for C₉H₁₅Cl (158.7): C, 68.13; H, 9.53. Found: C, 68.69; H, 9.56.

5-Chloro-3-methyl-1,3(E,Z)-pentadiene 2 (1.17 g, 10.0 mmol) and isobutene (3.43 g, 61.1 mmol) gave 1.10 g (64%) of 7-chloro-3,7-dimethyl-1,3(E,Z)-octadiene 7. - bp 30 - 35°C (bath)/0.2 mbar. - ^{1}H NMR (CCl₄, 90 MHz) of (E),(Z)-mixture: δ 1.55 (s, 6 H, C(CH₃)₂Cl), 1.73 (br. s, 3-CH₃), 1.69 - 1.93 (m, 6-H), 2.14 - 2.62 (m, 2 H, 5-H), 4.77 - 5.58 (m, 3 H, 1-H, 4-H), 6.07 - 6.85 (m, 1 H, 2-H). - Mass spectrum (79 eV): m/z - 174, 172 (9%, 30%, M⁺), 136 (12), 121 (40), 107 (23), 93 (89), 81 (100), 79 (70). - Anal. Calcd for C₁₀H₁₇Cl (172.7): C, 69.55; H, 9.92. Found: C, 69.34; H, 9.90.

1-Chloro-2,4-hexadiene 3 (0.58 g, 5.00 mmol, 4:1 mixture with 5-chloro-1,3-hexadiene) and isobutene (1.12 g, 20.0 mmol) yielded 0.620 g (72%) of a 10:1 mixture of 8a and 8b. - bp 25 - 33°C(bath)/0.1 mbar. - 8-Chloro-8-methyl-2(E),4(E)-nonadiene 8a: ^{1}H NMR (CDCl₃, 200 MHz): δ 1.57 (s, 6 H, C(CH₃)₂Cl), 1.73 (d, J - 7.0 Hz, 3 H, 1-H), 1.75 - 2.05 (m, 2 H, 7-H), 2.17 - 2.32 (m, 2 H, 6-H), 5.46 - 5.68 (m, 2 H, 2,5-H), 5.94 - 6.14 (m, 2 H, 3,4-H). - Mass spectrum (70 eV): m/z -

174, 172 (3%, 9%, M⁺), 121 (17), 107 (12), 93 (36), 81 (100), 79 (24). - **Anal.** Calcd for C₁₀H₁₇Cl (172.7): C, 69.55; H, 9.92. Found: C, 69.89; H, 9.95. - **7-Chloro-5,7-dimethyl-1,3(E)-octadiene 8b** the minor component of the mixture obtained above was identified by the ¹H NMR absorptions at δ 1.08 (d, J - 6.8 Hz, 5-CH₃), 2.42 - 2.66 (m, 6-H), 4.94 - 5.15 (m, -CH₂) and by the ¹³C NMR absorptions listed in Table 3.

6-Chloro-2,4-heptadiene 4 (0.65 g, 5.00 mmol) and isobutene (1.12 g, 20.0 mmol) reacted within 5 h to give 0.740 g (79%) of a 30:1 mixture of **9a** and **9b** with bp 28 - 33°C (bath)/0.1 mbar.- **8-Chloro-6,8-dimethyl-2,4-nonadiene 9a** (predominantly (E),(E)-isomer): ¹H NMR (CDCl₃, 200 MHz): δ 1.06 (d, J - 6.8 Hz, 3 H, 6-CH₃), 1.56, 1.58 (2s, each 3 H, C(CH₃)₂Cl), 1.72 (d, J - 5.8 Hz, 3 H, 1-H), 1.83 (d, J - 5.9 Hz, 2 H, 7-H), 2.39 - 2.61 (m, 1 H, 6-H), 5.37 - 5.73 (m, 2 H, 2,5-H), 5.91 - 6.07 (m, 2 H, 3,4-H). - Mass spectrum (70 eV): m/z - 188, 186 (2%, 6%, M⁺), 135 (15), 107 (18), 95 (100), 93 (11), 79 (12), 67 (26). - **Anal.** Calcd for C₁₁H₁₉Cl (186.7): C 70.76; H, 10.26. Found: C, 70.82, H, 10.29. - The minor component **4-Chloro-2-methyl-propyl)-2(E),5(E)-heptadiene 9b** was identified by the ¹³C NMR resonances listed in Table 3.

5-Chloro-1,3-cycloheptadiene 5 (32.0 mmol ≙ 5.14 g of a mixture containing 20% of the unreactive 6-chloro-1,3-cycloheptadiene) and isobutene (3.37 g, 60.0 mmol) gave 5.35 g (91%) of a 1:3 mixture of 5-(2-chloro-2-methyl-propyl)-1,3-cycloheptadiene **10a** and 3-(2-chloro-2-methyl-propyl)1,4-cycloheptadiene **10b** with bp 41 - 43°C (bath)/0.01 mbar. - ¹H NMR (CCl₄, 60 MHz): δ 1.61 (s, C(CH₃)₂Cl), 1.83 (d, J - 5 Hz, CH₂-CCl of **10a**), 2.03 (d, J - 6 Hz, CH₂-CCl of **10b**), 2.25 (mc, CH₂-CH₂), 2.66 (mc, 5-H of **10a**), 3.42 (mc, 3-H of **10b**), 5.23 - 5.95 (m, Vinyl-H). - Mass spectrum (90 eV): m/z - 186, 184 (1%, 2%, M⁺), 133 (100).

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