

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

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Abstract: The dienyllic 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].

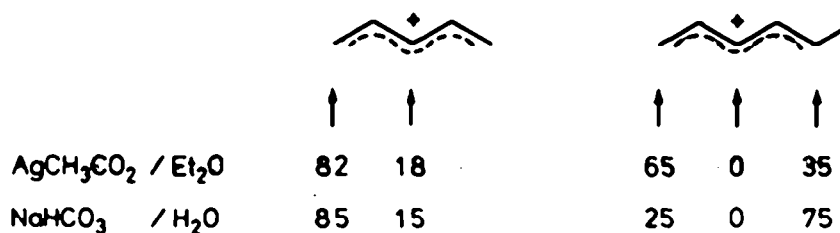
Scheme 1^{2b}

	$\text{CH}_2\text{-CH}^{\ominus}\text{-CH-CH-CH}_2$		$\text{CH}_2\text{-CH}^{\ominus}\text{-CH-CH-CH(CH}_3\text{)}$			$\text{CH}_2\text{-CH-C(CH}_3\text{)}^{\ominus}\text{-CH-CH}_2$			
	↑	↑	↑	↑	↑	↑	↑	↑	↑
H ⁺	100	0	100	0	0	100	0	0	100
CH ₃ I	65	35	62	8	30	85	15	10	90

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 dienyllic 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 dienyllic alcohols [3,4a] and from the results of solvolysis reactions [4].

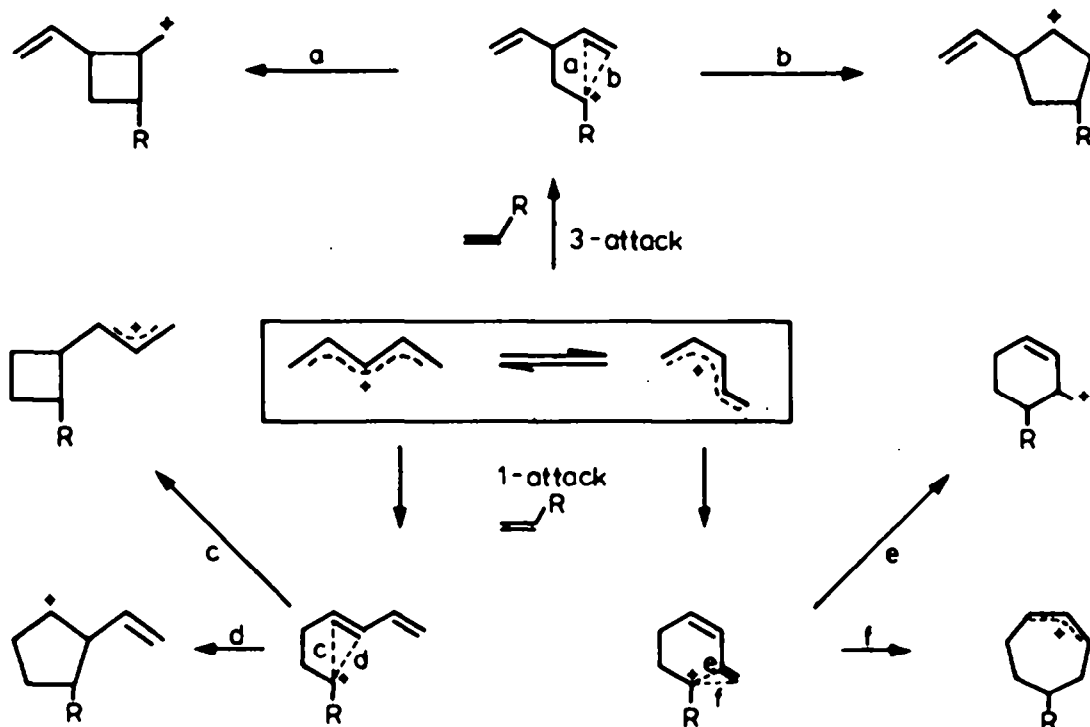
Miginlac reported that treatment of 5-chloro-1,3-pentadiene with silver acetate in ether or with aqueous bicarbonate solution yields 1,3-diene derivatives predominantly (Scheme 2) [4a]. Under the same conditions, conjugated dienes were formed exclusively from various hexadienyl cation precursors, i.e., 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}

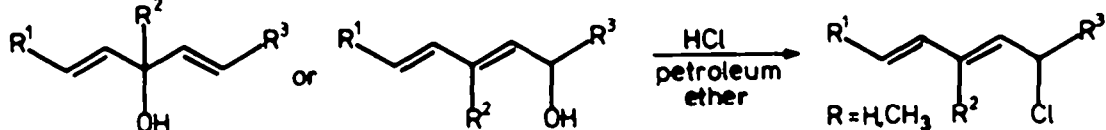
In contrast to noncoordinated dienyl cations, the corresponding transition metal complexes have also been studied with respect to their reactivity towards carbon nucleophiles. Whereas tri-carbonyldienyliron salts react exclusively at the dienyl termini [5a,b], the *n*¹ complexes with Pd, Mo and W are 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 cyclization 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. Dienyl 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 12*N* aqueous hydrochloric acid.

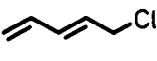
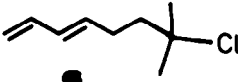
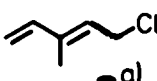
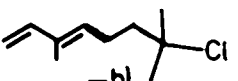
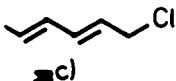
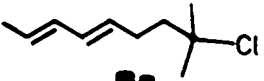
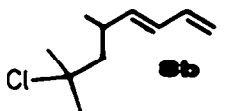

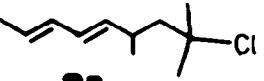
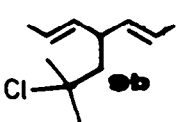
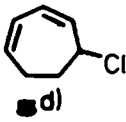
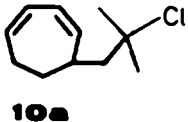
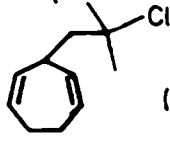
Table 1. ^{13}C NMR Chemical Shifts of the Chlorodienes 1 - 5

	R^1	R^2	R^3	C-1	C-2	C-3	C-4	C-5	R^1	R^2	R^3
1	H	H	H	119.12	135.50	134.72	128.71	44.80	-	-	-
(E)-2	H	CH_3	H	114.59	140.10	139.12	126.53	40.64	-	11.59	-
(Z)-2	H	CH_3	H	116.93	132.05	137.82	124.72	39.66	-	19.77	-
(E),(E)-3	CH_3	H	H	130.15	131.83	134.74	125.55	45.49	18.16	-	-
(E),(E)-4	CH_3	H	CH_3	130.17	131.83 ^a	131.39 ^a	131.53 ^a	58.41	18.17	-	25.31
5	$\text{R}^1, \text{R}^2 = \text{CH}_2, \text{CH}_2, \text{R}^3 = \text{H}$			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 $\text{C}(\text{CH}_3)_2\text{Cl}$ fragments and exclude the formation of cyclized products. The ^{13}C NMR data (Table 3) support the structural assignments.

Table 2. Zinc Chloride Catalyzed Additions of the Dienyl Chlorides 1 - 5 with Isobutene in CH_2Cl_2 , at -78°C .

Dienyl Chloride	[Isobutene] / [Dienyl Chloride]	Time (h)	Products	Yield (%)
	1.2	76		65
	6.1	144		64
	4.0	17		72 (~10:1)
				
	4.0	5		79 (~30:1)
				
	1.9	2		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 ³	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 ^a	130.58 ^b	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 34.33	22.94
9a	CH ₃	H	CH ₃	127.25	131.57	128.67	138.16	34.39	52.78	71.30	32.38 33.76	18.02 23.20
10a	R ¹ , R ² -CH ₂ -CH ₂	R ² -H	R ² -H	133.99	124.80 ^b	123.58 ^b	138.90	37.59	52.12	**	32.73 ^b 33.49 ^b	28.79 **
9b	CH ₃	H	CH ₃	124.19	135.21	43.17	135.21	124.19	50.88	**	33.15	**
10b	R ¹ , R ² -CH ₂ -CH ₂	R ² -H	R ² -H	129.20	135.48	34.95	135.48	129.20	52.99	70.80	33.00	25.97

** Signal covered.

^a Assignments uncertain.

Table 2 shows that the reaction times roughly decrease with increasing alkyl substitution of the dienylic 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 (\rightarrow isobutene polymerization) and (ii) electrophilic attack of the dienylic 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 dienylic derivatives [4b] and our previous studies on the relationship between $S_{\text{N}}1$ 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				C-1	Formal charges			ΔH_f° (kcal/mol)
	c ₁	c ₂	c ₃	c ₄ /c ₁		C-3	C-5		
	-0.517	+0.680	-0.517	1.32	0.243 (0.257)	0.326 (0.397)	0.243 (0.257)	219.7 (215.1)	
	-0.496	+0.692	-0.496	1.40	0.227 (0.229)	0.307 (0.393)	0.228 (0.222)	215.0 (210.4)	
	-0.546	+0.664	-0.488	1.21	0.214 (0.324)	0.312 (0.376)	0.225 (0.219)	207.3 (196.4)	
	-0.517	+0.653	-0.517	1.26	0.196	0.300	0.196	195.1	
	-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 delocalized 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_3/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 dienyl cations with isobutene can be rationalized on the basis of steric effects.

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EXPERIMENTAL

¹H NMR spectra: JNM-C-60-HL (JEOL), EM-390 and XL-200 (Varian). ¹³C 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. - ¹H 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 C₈H₁₃Cl (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. - ¹H 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 C₁₁H₁₇Cl (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: ¹H 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 C₁₁H₁₁Cl (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 C₁₁H₁₁Cl (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 (m, CH-CH₂), 2.66 (m, 5-H of 10a), 3.42 (m, 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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