253. Mesomeric Vinyl Cations. Part II.
Solvolysis of 2-Bromo-1, 3-Butadienes

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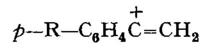
(13 X 70)

Summary. In contrast to 2-bromo-1,3-butadiene (**5**), the di-, tri- and tetramethyl derivatives **6–11** show remarkable solvolytic reactivity. First order rate constants and products of these bromodienes in 80% ethanol have been determined. Rates are very sensitive to the ionising power of the solvent but are not affected by triethylamine. Three types of products are formed, *i.e.* alkenynes, α,β-unsaturated ketones and 4-ethoxyallenes.

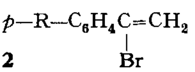
One methyl group on C-4 of **5** increases the reaction rate by a factor of ca. 10^2; two methyl groups increase the rate by ca. 10^4. Methyl substituents at C-1 have only a slight influence, apparently as a result of a rate-decreasing polar effect and a compensating rate-increasing steric effect.

The results of this study are consistent with a unimolecular ionization mechanism involving a mesomeric vinyl cation **12a** ↔ **12b** as an intermediate.

Since our original demonstration that vinyl cations **1** are intermediates in the solvolysis of certain *p*-substituted α-bromostyrenes **2** [1], numerous examples of the formation of disubstituted or digonal carbonium ions **3** in the solvolysis of activated vinyl halides and sulfonates **4** (X = halogen or RSO_3) have been reported¹). In all cases the derived vinyl cations **3** were stabilized by an electron-releasing α-aryl (**3a**) or α-cyclopropyl substituent (**3b**).


$p\text{-}R\text{-}C_6H_4\overset{+}{C}{=}CH_2$

1


$p\text{-}R\text{-}C_6H_4\underset{Br}{C}{=}CH_2$

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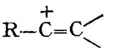

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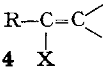
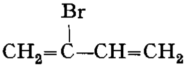


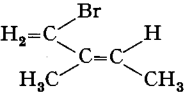
4

a) R = aryl;
b) R = cyclopropyl;
c) R = alkenyl

In Part I it was suggested that the extreme inertness of vinyl halides to ionization reactions of the S_N1 type might be overcome by electron release from a second,


$CH_2{=}\overset{Br}{C}{-}CH{=}CH_2$

5



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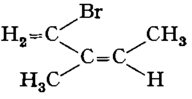

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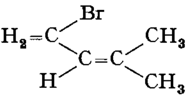

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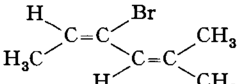

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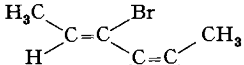

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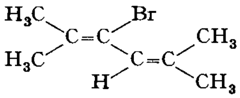

11

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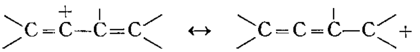
¹) Excellent reviews on vinyl cations in solvolysis reactions have recently appeared [2].

conjugated double bond as in 2-halo-1,3-dienes **4c**. This has now been confirmed by a study of reaction rates and products of the series of 2-bromo-1,3-dienes **5–11** in 80% ethanol²).

Since 2-bromo-1,3-butadiene (**5**) is known to lack solvolytic reactivity even at elevated temperatures, attention was directed primarily to its methyl derivatives. The well known electron-releasing effect of the methyl group was expected to increase the reactivity of bromodienes by stabilizing the mesomeric 2-dienyl cation **12a**↔**12b** formed in the rate-determining ionization step.

12a



12b

It was of particular interest to determine the influence on rate of methyl substituents in different positions of the 2-bromodiene. Consequently, the di-, tri- and tetra-methylated derivatives **6–11** were selected for study. The pairs of bromodienes **6** and **7**, and **9** and **10**, respectively, are *cis-trans* isomers. Their behaviour was therefore expected to shed light on the influence of stereochemical factors.

Syntheses. – The cis-trans *isomeric* **2**-*bromo*-**3**-*methyl*-**1**,**3**-*pentadienes* **6** *and* **7** were prepared by a known procedure [4]. Their configurations were assigned on the basis of their UV. absorption, *i.e.* the *trans* configuration for the isomer **6** (λ_{max} 229 nm, $\varepsilon = 17000$) and the *cis* configuration for the isomer **7** (λ_{max} 195 nm, $\varepsilon = 8100$). Models reveal considerable steric interaction between the bromine atom and the C-4 methyl group in the *cis*-isomer **7**, which results in a deviation from planarity and a concomitant hypsochromic shift.

2-*Bromo*-**4**-*methyl*-**1**,**3**-*pentadiene* (**8**) was prepared by the addition of HBr to 4-methyl-3-penten-1-yne (**13a**). The low extinction ($\varepsilon = 7500$) at 227 nm indicates the preponderance of the less hindered *s-cis* conformation (see below).

$$(CH_3)_2C{=}CH{-}C{\equiv}C{-}R \qquad \mathbf{13} \quad \begin{matrix} \mathbf{a)}\ R = H \\ \mathbf{b)}\ R = CH_3 \end{matrix}$$

cis- (**9**) *and* trans-**3**-*Bromo*-**5**-*methyl*-**2**,**4**-*hexadienes* (**10**) were obtained in a 1:1 ratio in 68% yield by addition of HBr to 2-methyl-2-hexen-4-yne (**13b**), which in turn was prepared by methylation of the sodium salt of **13a** with methyl iodide. The resulting isomeric bromodienes **9** and **10** were separated by gas chromatography and their configurations established by NMR. and UV. spectroscopy. Since vinylic protons *cis* to bromine resonate at lower field than *trans* protons³) and since the quartets of the C-2 protons of **9** and **10** are centered at 5.95 and 5.74 ppm, respectively, the former must have the *cis* configuration. The relative positions of the doublets due to the C-1 methyl groups are reversed and are located at 1.53 and 1.80 ppm, respectively, in the NMR. spectra of **9** and **10**. These assignments are supported by the hypsochromic shift of the UV. absorption of **9** to 208 nm compared to 215 nm for **10**. This is due to additional steric hindrance between the C-1 and C-4 methyl groups in **9**, which is absent in the *trans* isomer **10**.

3-*Bromo*-**2**,**5**-*dimethyl*-**2**,**4**-*hexadiene* (**11**) was first obtained in the following manner: Addition of bromine to β-methyl-crotonaldehyde (**14**) led to 2,3-dibromo-3-

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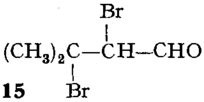
²) A preliminary account of this work has been published [3].

³) *E.g.* the *cis* and *trans* vinylic protons in 2-bromopropene $CH_2{=}C(Br)CH_3$ give rise to signals at 5.52 and 5.33 ppm, respectively [5].

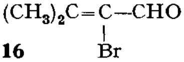
methyl-butanal (**15**), which upon treatment with potassium acetate yielded unstable 2-bromo-3-methyl-2-butenal (**16**). This was treated with isopropyl-magnesium bromide and the resulting 4-bromo-2,5-dimethyl-4-hexen-3-ol (**17a**) dehydrated with the usual agents[4]). These attempts invariably led to 3-bromo-2,5-dimethyl-1,3-hexadiene (**18**), an isomer of the required bromodiene **11**. However, pyrolysis at 470° of the acetate **17b** of the alcohol **17a** afforded a 7% yield of **11** besides 26% of the isomeric bromodiene **18**[5]).

$(CH_3)_2C{=}CH{-}CHO$

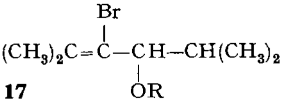
14


$(CH_3)_2C(Br){-}CH(Br){-}CHO$

15

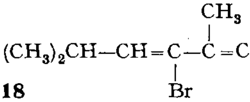

$(CH_3)_2C{=}C(Br){-}CHO$

16


$(CH_3)_2C{=}C(Br){-}CH(OR){-}CH(CH_3)_2$

17

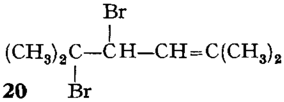
a) $R = H$
b) $R = COCH_3$


$(CH_3)_2CH{-}CH{=}C(Br){-}C(CH_3){=}CH_2$

18

$(CH_3)_2C{=}CH{-}CH{=}C(CH_3)_2$

19

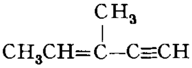

$(CH_3)_2C(Br){-}CH(Br){-}CH{=}C(CH_3)_2$

20

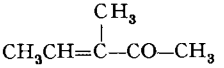
A practical synthesis of 3-bromo-2,5-dimethyl-2,4-hexadiene (**11**) was finally achieved by brominating 2,5-dimethyl-2,4-hexadiene (**19**) and heating the resulting crude dibromide **20** with potassium *t*-butoxide. Fractional distillation on a spinning band column yielded pure bromodiene **11** in 19% yield. The latter was identified by its NMR. spectrum which showed signals at 1.60, 1.67, 1.77 and 1.88 ppm, corresponding to four methyl groups, and one signal due to the vinylic proton at 5.68 ppm. The UV. absorption maximum at 210 nm indicates considerable distortion of the diene system.

Results. – The bromodienes **6–11** were solvolysed in 80-vol.% ethanol containing 1.2 molar equivalents of triethylamine to suppress secondary reactions due to the HBr generated in the process. The solvolyses of **8**, **9**, **10** and **11** were conducted at 100°, while the less reactive compounds **6** and **7** were run at 150°. Products were separated and determined quantitatively by gas chromatography. Known compounds were identified by comparison with authentic samples, new compounds by elemental analyses and by spectroscopic methods.

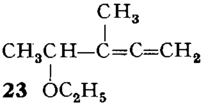
2-Bromo-1,3-butadiene (**5**) underwent extensive polymerisation which precluded the isolation of products. 2-Bromo-3-methyl-1,3-pentadiene (**6**), however, yielded 3-methyl-3-penten-1-yne (**21**) (20%), 3-methyl-3-penten-2-one (**22**) (25%) and 4-ethoxy-3-methyl-1,2-pentadiene (**23**) (55%). The IR. spectrum of the latter showed characteristic allene absorption at 1961 cm^{-1}. In the case of the *cis*-isomer **7** the yields of the three products **21**, **22** and **23** were 16%, 21%, and 63%, respectively.


$CH_3CH{=}C(CH_3){-}C{\equiv}CH$

21


$CH_3CH{=}C(CH_3){-}CO{-}CH_3$

22


$CH_3CH(OC_2H_5){-}C(CH_3){=}C{=}CH_2$

23

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[4]) *E.g.* $SOCl_2$ or PBr_3 in pyridine and 1,5-diazabicyclo[4.3.0]-non-5-ene, acetic anhydride, *p*-toluenesulfonic acid, oxalic acid.

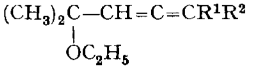
[5]) The bromodiene **18** is also exclusively formed in the *Chugaev* reaction of the alcohol **17a**.

From 2-bromo-4-methyl-1,3-pentadiene (**8**) 4-methyl-3-penten-1-yne (**13a**) (29%), mesityl oxide (**24a**) (16%) and 4-ethoxy-4-methyl-1,2-pentadiene (**25a**) (55%) were isolated.

Solvolysis of *cis*-3-bromo-5-methyl-2,4-hexadiene (**9**) led to 2-methyl-2-hexen-4-yne (**13b**) (24%), 5-methyl-4-hexen-3-one (**24b**) (23%), and 5-ethoxy-5-methyl-2,3-hexadiene (**25b**) (53%). From the *trans*-isomer **10** the same compounds were obtained in yields of 19%, 28%, and 53%, respectively. Solvolysis of the 1:1 mixture of *cis*- and *trans*-3-bromo-5-methyl-2,4-hexadiene, **9** and **10** respectively, yielded a 1:1 mixture of stereoisomeric allene ethers **25b**, inseparable by gas chromatography. The presence in the NMR. spectrum of two doublets ($J = 6.5$ cps) of equal intensity, corresponding to two kinds of allenic methyl groups ($C=C=CHCH_3$), proves that the configurations of the substituents about the 2,3-double bonds in the bromodienes **9** and **10** are preserved during the reaction.

$(CH_3)_2C=CH-CO-CH_2R$

24 a) $R = H$
b) $R = CH_3$



$$\underset{\displaystyle OC_2H_5}{(CH_3)_2C-CH}=C=CR^1R^2$$

25 a) $R^1 = R^2 = H$
b) $R^1 = H;\ R^2 = CH_3$
c) $R^1 = R^2 = CH_3$

Finally, solvolysis of 3-bromo-2,5-dimethyl-2,4-hexadiene (**11**) afforded 5-ethoxy-2,5-dimethyl-2,3-hexadiene (**25c**) as the only product. The two allenic methyl groups R^1 and R^2 in **25c** give rise to two distinct signals at 1.63 and 1.68 ppm.

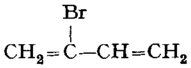
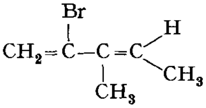
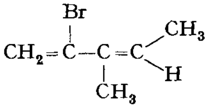
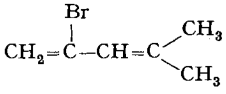
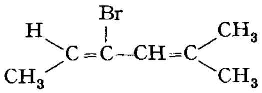
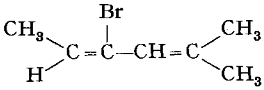
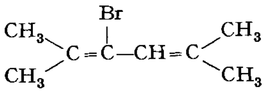
The relative amounts of products isolated from the bromodienes **6–11** are summarized in Table 1. They vary with reaction time, since the allene ethers are gradually hydrolysed to α,β-unsaturated ketones. The yields therefore apply only to the conditions described in the experimental section.

Table 1. *Reaction products (in %) of 2-bromo-1,3-dienes in 80-vol.-% ethanol containing 1.2 molar equiv. of triethylamine*

Compound	Temp. °C	$-C\equiv C-\overset{|}{C}=C\langle$	$\rangle CHCO\overset{|}{C}=C\langle$	$\rangle C=C=\overset{|}{C}-\overset{|}{\underset{|}{C}}-OC_2H_5$
6	150°	20	25	55
7	150°	16	21	63
8	100°	29	16	55
9	100°	24	23	53
10	100°	19	28	53
11	100°	–	–	100

The first order rate constants of the bromodienes **5–11** were determined in 80-vol.% ethanol in the presence of 1.2 equivalents of triethylamine and are listed in Table 2. In separate runs it was shown that the rate constants were not affected by a fourfold excess of the base. The reactions of compounds **8–11** were followed conductometrically, and those of the less reactive bromodienes **5**, **6** and **7** by titration of bromide ion. Activation parameters, which were calculated from rate measurements at three temperatures, are also listed in Table 2. Relative rates are correlated with observed and calculated UV. absorption maxima in Table 3.

Table 2. *First order rate constants in 80-vol.% ethanol, c = ca. 10^{-3} M, with 1.2 to 4.8 molar equivalent of triethylamine*

		Temp. °C	k(s^{-1})	E^* kcal	S^* cal/°C
(5)	 $CH_2{=}C(Br){-}CH{=}CH_2$	150.0	$1.5\ \times10^{-6}$[a]		
(6)	 $CH_2{=}C(Br){-}C(CH_3){=}C(H)(CH_3)$	100.0	1.55×10^{-6}[b]	26.6	−16.2
		130.0	2.30×10^{-5}		
		140.0	4.95×10^{-5}		
		150.0	1.11×10^{-4}		
(7)	 $CH_2{=}C(Br){-}C(CH_3){=}C(CH_3)(H)$	100.0	3.08×10^{-6}[b]	25.6	−17.2
		130.0	4.05×10^{-5}		
		140.0	9.17×10^{-5}		
		150.0	1.83×10^{-4}		
(8)	 $CH_2{=}C(Br){-}CH{=}C(CH_3)_2$	70.0	4.75×10^{-5}[b][c]		
		90.0	3.25×10^{-4}		
		100.0	8.29×10^{-4}[d]	24.0	−10.9
		110.0	1.84×10^{-3}		
(9)	 $(H)(CH_3)C{=}C(Br){-}CH{=}C(CH_3)_2$	90.0	4.64×10^{-4}		
		100.0	1.11×10^{-3}	23.3	−12.1
		110.0	2.50×10^{-3}		
(10)	 $(CH_3)(H)C{=}C(Br){-}CH{=}C(CH_3)_2$	90.0	1.77×10^{-4}		
		100.0	4.61×10^{-4}	24.9	− 9.6
		110.0	1.07×10^{-3}		
(11)	 $(CH_3)_2C{=}C(Br){-}CH{=}C(CH_3)_2$	80.0	1.45×10^{-4}		
		90.0	4.66×10^{-4}		
		100.0	1.18×10^{-3}	24.1	− 9.8
		110.0	2.66×10^{-3}		

[a] calc. from initial slope

[b] extrapolated

[c] in 50-vol.% ethanol at 70°, $k = 3.66\times10^{-3}$ s^{-1}

[d] with 0 to 4 molar equiv. of triethylamine.

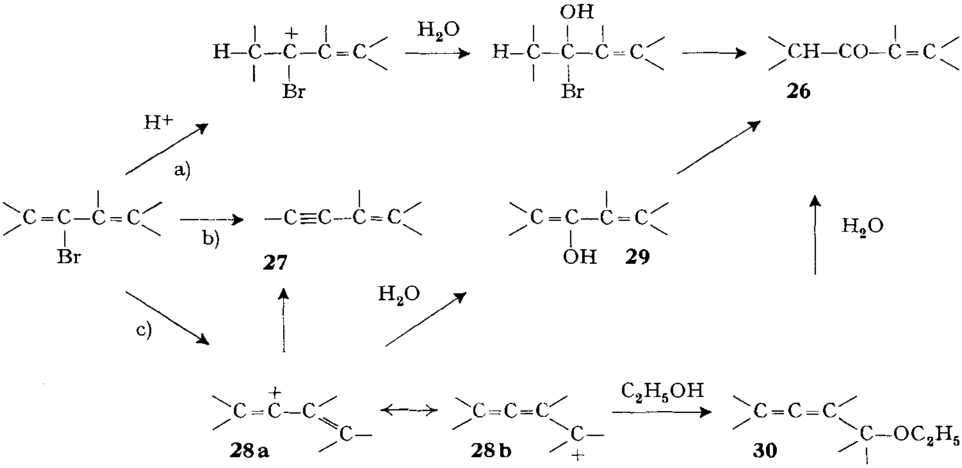
Table 3. *Relative rate constants and UV. absorption*[a] *of 2-bromodienes*

Compound	$k_{\mathrm{rel}}^{100°}$	λ_{max} obs.	λ_{max} calc.[b]	ε
(5)	ca. 0.01	219	–	–
(6)	1	229	229	17000
(7)	2	195	229	8100
(8)	535	227	229	7500
(9)	715	208	234	8400
(10)	298	215	234	7660
(11)	762	210	239	13000

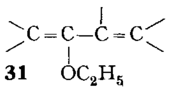
[a] in ethanol.

[b] based on **5** and an increment of 5 nm per methyl substituent and per bromine.

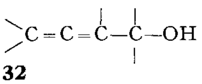
Discussion. – With the exception of the readily polymerisable 2-bromo-1,3-butadiene (**5**), the low reactivity of which precluded a detailed study, all bromodienes were shown to react by a unimolecular mechanism. The insensitivity of rates to added triethylamine excludes the acid-catalysed hydration process (path a) leading to an α,β-unsaturated ketone **26**. Also excluded is the base-induced elimination to an alkenyne **27** (path b). In fact rates and products are explicable only on the basis of the ionisation mechanism (path c) involving a mesomeric vinyl cation **28a** ↔ **28b**. This is supported by the high sensitivity of reaction rate to the ionizing power of the solvent, since the bromodiene **8** reacted 77 times faster in 50% ethanol than in 80% ethanol (Table 2). This factor corresponds to a *m*-value of approximately 1 in the *Grunwald-Winstein* equation [6] and indicates an ionization process of the limiting type [7].



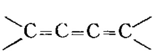
Since the mesomeric vinyl cation **28a** ↔ **28b** contains two electrophilic centres, *i.e.* C-2 and C-4, reaction with solvent leads to α,β-unsaturated ketones **26** (*via* 2-hydroxybutadienes **29**) as well as to 4-ethoxyallenes **30**. The latter are the dominant products from all bromodienes and the sole product from **11** (Table 1). As mentioned above, 4-ethoxy-allenes **30** undergo hydrolysis to α,β-unsaturated ketones **26**. The yields listed in Table 1 therefore represent a lower limit. Finally, loss of a proton from the cation **28a** ↔ **28b** leads to alkenynes **27**.


$>C=C-C(OC_2H_5)=C<$

31


$>C=C=C-C-OH$

32


$>C=C=C=C<$

33

2-Ethoxy-1,3-butadienes (**31**) and 1-hydroxy-2,3-butadienes (**32**) were not detected among the products, although water and ethanol would be expected to attack at both electrophilic centers of the mesomeric cation **28a** ↔ **28b**[6]). Possibly, the very labile enol ethers **31** undergo hydrolysis under the reaction conditions. There was also no indication that 1,2,3-butatrienes **33** were formed by loss of a proton from C-3 of the cation **28**.

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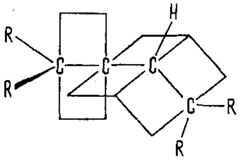
[6]) The selectivity of cationic centers towards the components of mixed nucleophilic solvents is little understood.

The relative solvolysis rates listed in Table 3 indicate that at least one methyl group is required on the terminale C-4 atom for facile ionization. Thus one methyl group, as in **6** and **7**, increases the rate by a factor of ca. 10^2 relative to 2-bromo-1,3-butadiene (**5**), whereas two geminal methyl groups as in **8**, **9**, **10**, and **11** increase the rate by ca. 10^4.

The large effect of methyl substituents on C-4 is readily explained by the ionisation mechanism (path c) because the greater part of the positive charge developed in the transition state will be transferred to the sp^2-hybridized C-4 atom[7]. However, charge delocalisation can only take place readily when the planes of the diene double bonds intersect at an angle of approximately 90°. Only then can the incipient p-orbital on C-2 overlap effectively with the π-orbital of the C-3,4 double bond as required by the mesomeric cation **34**. In addition sp-hybridisation of C-2 in the allene-like structure **34** requires a linear arrangement of C-1, -2 and -3[8].



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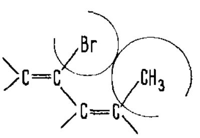
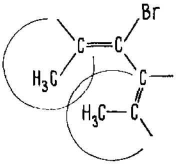
It follows from these considerations that the bromodienes should react most readily in a non-planar conformation. The UV.-absorption maxima listed in Table 3 indicate that considerable departure from planarity must already occur in the ground states of the bromodienes **7**, **9**, **10** and **11**, since the maxima are shifted to shorter wave-lengths by 19 to 34 nm relative to calculated values. This departure from planarity is mainly due to steric hindrance between the bromine atom on C-2 and the *cis*-methyl group on C-4 in the *s-trans* conformation **35** and between *cis*-methyl groups on C-1 and C-4 in the *s-cis* conformation **36**.



35



36

Part of the rate increasing effect of a *cis*-methyl substituent on C-4 should therefore be ascribed to steric hindrance of planarity which raises the ground state energy of the bromodiene. This is borne out by the fact that the twisted bromodiene **7** (λ_{max} 195 nm, $\varepsilon = 8100$) reacts twice as fast as the planar isomer **6** (λ_{max} 229 nm, $\varepsilon = 17000$) (Table 3).

A surprising result illustrated by the relative rates of compounds **8**–**11** (Table 3) is the fact that one or two methyl groups on C-1 influence reactivity only slightly and

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[7] This effect of C-4 methyl groups is reminiscent of the enormous rate enhancement caused by 3-methyl substituents in allylic halides; cf. [8].

[8] The geometry of mesomeric vinyl cations of the type **28a** ↔ **28b** is discussed in the following article of this series.

even lead to a small rate depression in the case of the compound **10**. This observation suggests that a methyl group on C-1 of the double bond actually decreases the ionization rate and that this effect is compensated by the steric effect when the C-1 methyl group is *cis* as in **9** and **11**.

The methyl group is commonly considered to be electron releasing relative to hydrogen, due to its inductive effect [9] or to hyperconjugation [10]. It appears that this effect may be negligible or even reversed when the methyl group is located on the β-carbon atom of a vinyl cation[9]). In view of the current controversy concerning the polar effects of alkyl groups relative to hydrogen[10]), these results merit further study.

Financial support from *CIBA Aktiengesellschaft*, Basel, and from the '*Schweizerischer Nationalfonds*' is gratefully acknowledged.

Experimental Section

Melting points (m.p.) were determined on a *Kofler* Block and are corrected; accuracy below 200°C ± 1°. Boiling points (b.p.) are uncorrected.

UV. spectra were measured on a *Beckman*-DB spectrophotometer, IR. spectra with a *Beckman* IR-8 instrument, and NMR. spectra with a *Varian*-A-60 spectrometer, using tetramethylsilane as an internal standard. Gas-chromatographic analyses were carried out with an *Aerograph*, Model HY-FI 600 B (*Wilkens*), and with an *Autoprep* A 700 (*Aerograph*) for separations on a preparative scale.

Syntheses. – cis- (**7**) *and* trans-*2-Bromo-3-methyl-1,3-pentadiene* (**6**) were prepared by the procedure described by *Traynard* [4]. The isomers were separated by destillation with a 25 cm spinning band column; *cis-* (**7**): b.p. 41°/32 Torr (Lit. [4]: 41°/32 Torr); *trans-* (**6**): b.p. 39°/10 Torr (Lit. [4]: b.p. 39°/10 Torr). The physical data were also in agreement with the literature [4].

2-Bromo-4-methyl-1,3-pentadiene (**8**). 16.0 ml (0.206 mol) of 63% aqueous HBr were added dropwise (2 h) to 10.0 g (0.125 mol) of 4-methyl-3-penten-1-yne (**13a**) [13] with stirring at – 10° to – 5°. After 3 h at room temperature 50 ml of water were added and the lower oily layer separated. This was washed with three 20 ml portions of water, with 20 ml 5% $NaHCO_3$ and finally with 20 ml of water. After drying over $CaCl_2$, the crude yellow oil was distilled on a 25 cm spinning band column in presence of a trace of hydroquinone, yielding 13.9 g (69%) of pure **8**, b.p. 58°/45 Torr. – UV. spectrum (ethanol): λ_{max} 227 nm (ε = 7500). IR. spectrum (CCl_4): 1610, 1650 cm^{-1} (diene), 885 cm^{-1} (=CH_2). NMR. spectrum in CCl_4 (ppm): 1.84 (*s*, 6 H), 5.48 (*d*, 1 H), 5.58 (*d*, 1 H), 5.75 (*m*, 1 H); long-range coupling causes further splitting of the main signals.

C_6H_9Br (161.05) Calc. C 44.8 H 5.6 Br 49.6% Found C 45.1 H 5.7 Br 49.3%

2-Methyl-2-hexen-4-yne (**13b**). To 3.03 g (0,132 mol) of sodium, powdered under xylene and suspended in 100 ml abs. tetrahydrofuran, a solution of 10.5 g (0.130 mol) 4-methyl-3-penten-1-yne (**13a**) [13] in 20 ml abs. tetrahydrofuran was added dropwise (45 min). The suspension was stirred at 22° for 2 h and heated under reflux for further 2 h. After cooling to 0°, 28.0 g (0.197 mol) of pure methyl iodide in 20 ml abs. tetrahydrofuran were added dropwise with stirring (45 min). After 30 min at 10° the mixture was heated under reflux for further 30 min. After cooling the reaction mixture, from which yellowish crystals had separated, was treated slowly with 200 ml of water, when a brown oily layer separated. This was extracted twice with 50 ml portions of ether. The combined extracts were washed, dried over $CaCl_2$ and evaporated to dryness after addition of a trace of hydroquinone. The brown residue yielded 8.3 g (67%) of **13b**, b.p. 56–58°/95 Torr, upon distillation through a *Vigreux* column (Lit. [14]: b.p. 56°/95 Torr). IR. spectrum in CCl_4 (cm^{-1}): 1632 (C=C), 1435, 1380 (CH_3). NMR. spectrum in CCl_4 (ppm): 1.78 (*d*, 3 H), 1.93 (*d*, 6 H), 5.18 (*m*, 1 H).

cis- (**9**) *and* trans-3-*Bromo-5-methyl-2,4-hexadiene* (**10**). 7.5 ml (0.0966 mol) of 63% aqueous HBr were added dropwise (60 min) with vigorous stirring to 5.5 g (0.0585 mol) of 2-methyl-2-

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[9]) According to recent molecular orbital calculations [11] a methyl group on the β-carbon atom of a vinyl cation provides no extra stabilization.

[10]) For a recent review see [12].

hexen-4-yne (**13b**) precooled to –10°. After further stirring at –10° or 1 h and at 20° for 2 h, the emulsion was diluted with 50 ml of water and then extracted with ether. The ether extract was washed with 50 ml portions of water and 5% aqueous $NaHCO_3$, then dried over $CaCl_2$ and evaporated to dryness. The residue, to which 100 mg of hydroquinone were added, was distilled through a *Vigreux* column, yielding 7.0 g of a mixture of **9** and **10**, b.p. 54°/14 Torr.

$C_7H_{11}Br$ (175.07) Calc. C 48.0 H 6.3 Br 45.6% Found C 48.2 H 6.4 Br 45.3%

The isomers were separated by preparative gas chromatography at 75° (6 m column packed with 5% Silicone rubber SE 52 and 3% Bentone 34 on Chromosorb G AW DM CS).

cis-*Isomer* **9**: UV. spectrum in ethanol: λ_{max} 208 nm (ε = 8400). IR. spectrum in CCl_4 (cm^{-1}): 1630, 1660 (diene), 1380, 1445 (CH_3). NMR. spectrum in CCl_4 (ppm): 1.53 (*d*, 3 H), 1.67, 1.82 (2 *s*, 6 H), 5.65 (*m*, 1 H), 5.95 (*q*, 1 H).

trans-*Isomer* **10**: UV. spectrum in ethanol: λ_{max} 215 nm (ε = 7600). IR. spectrum in CCl_4 (cm^{-1}): 1664, 1660 (diene), 1445, 1375 (CH_3). NMR. spectrum in CCl_4 (ppm): 1.78 (*s*, 6 H), 1.80 (*d*, 3 H), 5.65 (*m*, 1 H), 5.74 (*q*, 1 H).

2-Bromo-3-methyl-2-butenal (**16**). To a cooled solution of 16.8 g (0.2 mol) β-methyl-crotonaldehyde (**14**) and 50 mg hydroquinone in 90 ml methylene chloride 32.0 g (0.4 mol) of bromine in 90 ml methylene chloride were added dropwise at 0° to 10° (30 min). Then 28.0 g (0.286 mol) of potassium acetate were added with further cooling and the resulting suspension stirred at room temperature for 24 h. After filtration the solution was concentrated *in vacuo* (12 Torr) and the residue steam-distilled. The aldehyde **16** separated as white crystals in the distillate after cooling to 0°. These were extracted with CH_2Cl_2 and recovered after drying the solution over $CaCl_2$ by evaporating to dryness. The unstable aldehyde **16**, 23.1 g (71%), liquefied at room temperature. UV. spectrum in ethanol: λ_{max} 258 nm (ε = 14500). IR. spectrum in CCl_4 (cm^{-1}): 2855, 2740, 1690 (CHO). – The *2,4-dinitrophenylhydrazone*, from ethanol, melted at 206°.

$C_{11}H_{11}BrN_4O_4$	Calc.	C 38.5	H 3.2	Br 23.4	N 16.3	O 18.6%
(343.144)	Found	,, 38.3	,, 3.3	,, 25.5	,, 16.2	,, 18.1%

4-Bromo-2,5-dimethyl-4-hexen-3-ol (**17a**). To the *Grignard* reagent from 13.6 g (0.559 mol) magnesium and 59.0 g (0.48 mol) of isopropyl bromide in 280 ml abs. ether a solution of 58.0 g (0.356 mol) 2-bromo-3-methyl-2-butenal (**16**) in 100 ml abs. ether was added dropwise with stirring and cooling to 0° (60 min). The suspension was stirred over night at 20° and then slowly poured into crushed ice and 2N H_2SO_4. After shaking, the ether layer was separated and washed with water, saturated aqueous $NaHSO_3$, again with water and finally with 50 ml 5% aqueous $NaHCO_3$. After drying over $CaCl_2$ the ether was evaporated *in vacuo* and the crystalline residue (58.0 g) recrystallized from petroleum ether. 31.1 g (42%) **17a** were obtained as white crystals, m.p. 71.5–72.0°. NMR. spectrum in CCl_4 (ppm): 0.73 (*d*, 3 H), 1.03 (*d*, 3 H), 1.63 (*s*, 1 H), 1.86 and 1.90 (2 *s*, 7 H), 3.80 (*d*, 1 H).

$C_8H_{15}BrO$	Calc.	C 46.4	H 7.3	Br 38.6	O 7.7%
(207.116)	Found	,, 46.4	,, 7.3	,, 39.3	,, 7.8%

Acetate **17b**: 10.0 g (0.0484 mol) of the alcohol **17a** and 16.0 g (0.157 mol) of acetic anhydride were heated at 105° for 60 min. After cooling 25 ml of water were added. The mixture was shaken at 50° for 5 min to hydrolyse the excess anhydride and then extracted with ether. The ether extract was washed twice with 20 ml water, twice with 20 ml 5% aqueous $NaHCO_3$ and dried over $CaCl_2$. The residue obtained after evaporation of the ether *in vacuo* was distilled through a *Vigreux* column to yield 8.6 g (72%) acetate **17b** as a colorless liquid, b.p. 103–104°/12 Torr. IR. spectrum in CCl_4 (cm^{-1}): 1738 (C=O), 1239 (acetate). NMR. spectrum in CCl_4 (ppm): 0.80 (*d*, 3 H), 0.97 (*d*, 3 H), 1.91 and 1.95 (2 *s*, 6 H), 2.02 (*s*, 3 H), ca. 2 (*m*, 1 H), 5.10 (*d*, 1 H).

$C_{10}H_{17}BrO_2$ (249.153) Calc. C 48.2 H 6.9 Br 32.1% Found C 48.4 H 6.8 Br 32.2%

3-Bromo-2,5-dimethyl-2,4-hexadiene (**11**). – a) *Pyrolysis of* **17b**. The apparatus [15] consisted of a Pyrex glass reaction tube, 40 cm long by 1.2 cm diameter, filled with glass beads of 3.5 mm diameter, mounted vertically in an electric furnace 21 cm long. Attached to the top of the tube were a dropping funnel and an inlet tube for nitrogen. – 4.0 g (0.016 mol) of acetate **17b** were added dropwise during 5 min at 470° while N_2 was passed through the tube (ca. 200 bubbles per min). In the receiver, cooled by an ice-salt bath, 3.4 g of a brown liquid were collected. This was taken up in ether and washed successively with water, 5% aqueous $NaHCO_3$ and again with water. After drying over $CaCl_2$ the ether solution was evaporated to dryness. The residue was mixed with ca. 50 mg of hydroquinone and distilled in a bulb tube at 80–90°/15 Torr. The colourless distillate, 2.1 g, was separated by preparative gas chromatography at 115° (6 m column packed with 10% Carbowax 20 M on Chromosorb W AW) into 2 fractions.

The first fraction consisted of 790 mg (26%) *3-bromo-2,5-dimethyl-1,3-hexadiene* (**18**). UV. spectrum in ethanol: λ_{max} 226 nm (ε = 17000). IR. spectrum in CCl_4 (cm^{-1}): 900 and 1800 ($=CH_2$), 1605 and 1620 (diene), 1370 and 1380 (gem. CH_3). NMR. spectrum in CCl_4 (ppm): 1.00 (*s*, 3 H), 1.10 (*s*, 3 H), 1.98 (*s*, 3 H), 2.85 (*m*, 1 H), 5.05 (*s*, 1 H), 5.44 (*s*, 1 H), 5.75 (*d*, 1 H).

$C_8H_{13}Br$ (189.101) Calc. C 50.8 H 6.9 Br 42.3% Found C 51.2 H 7.1 Br 43.2%

The second fraction consisted of 212 mg (7%) *3-bromo-2,5-dimethyl-2,4-hexadiene* (**11**). UV. spectrum in ethanol: λ_{max} 210 nm (ε = 13000). NMR. spectrum in CCl_4 (ppm): 1.60 (*d*, 3 H), 1.67 (*d*, 3 H), 1.77 (*d*, 3 H), 1.88 (*d*, 3 H), 5.68 (*m*, 1 H).

$C_8H_{13}Br$ (189.101) Calc. C 50.8 H 6.9 Br 42.3% Found C 50.8 H 6.9 Br 42.0%

b) *From 2,5-dimethyl-2,4-hexadiene* (**19**). To a solution of 55.0 g (0.5 mol) of 2,5-dimethyl-2,4-hexadiene (commercial grade) in 320 ml pentane 80.0 g (0.5 mol) of bromine were added between 0° and 5° (30 min) with stirring. Then 100 g (0.89 mol) of potassium *t*-butoxide were added within 5 min, causing an initial rise in temperature to ca. 35°. Stirring was continued for 36 h at 22°. 500 ml of water were then slowly added to the reaction mixture and the pentane layer separated after thorough shaking. The pentane extract was washed with water, 1 N HCl and again with water, dried over $CaCl_2$ and evaporated to dryness *in vacuo*. The liquid residue was distilled and yielded 41 g of a fraction b. 41–86°/15 Torr. Redistillation through a spinning band column gave 17.6 g (19%) of pure **11**, b.p. 49–50°/8 Torr, identical with the substance obtained by procedure a).

Preparative Solvolyses. – *General procedure.* 0.1 M solutions of the bromodienes **6–11** in 80-vol.% ethanol, containing 1.2 equiv. of triethylamine, were heated in sealed glass tubes as specified below. After cooling, the reaction solution was carefully acidified with 2 N HCl, diluted with the sixfold volume of water and extracted with twice the original volume of pentane. The pentane extracts were dried over $CaCl_2$ and concentrated to a volume of ca. 2 ml by distillation through a *Vigreux* column. The products were analysed or separated by gas chromatography with helium on either one of the following columns: a) 3% Bentone 34 and 5% Silicone rubber SE 52 on Chromosorb G AW DMCS; b) 15% Carbowax 20 M on Chromosorb W AW. Peak areas were determined by the method of *Condal-Bosch* [16]. Each measurement was repeated at least once (accuracy ± 4%).

trans *2-Bromo-3-methyl-1,3-pentadiene* (**6**). 1.61 g (0.010 mol) **6** in 100 ml 80-vol.% ethanol (0.12 molar in triethylamine) were heated to 100° for 14 h. Gas-chromatographic analysis on column a) at 110° showed the presence of 20% *3-methyl-3-penten-1-yne* (**21**) and 25% *3-methyl-3-penten-2-one* (**22**), which were identified by comparison of retention volumes and spectra with those of authentic samples. The third component of the product mixture consisted of 55% *4-ethoxy-3-methyl-1,2-pentadiene* (**23**). IR. spectrum in CCl_4 (cm^{-1}): 1961 (C=C=C), 1440, 1370 (CH_3). NMR. spectrum in CCl_4 (ppm): 1.13 (*d*, 3 H), 1.58 (*t*, 3 H), 3.32 (*q*, 2 H), 3.85 (*q*, 1 H), 4.55 (*q*, 2 H).

$C_8H_{14}O$ (126.20) Calc. C 76.14 H 11.18% Found C 76.35 H 11.21%

cis-*2-Bromo-3-methyl-1,3-pentadiene* (**7**). Analogous reaction of 1.61 g (0.01 mol) **7** at 100° for 8 h led to 16% **21**, 21% **22** and 63% **23**.

2-Bromo-4-methyl-1,3-pentadiene (**8**). 1.0 g (6.5 mmol) of **8** in 65 ml 80-vol.% ethanol (0.12 molar in triethylamine) was heated to 100° for 112 min. Gas-chromatography on column b) showed the presence of 29% *4-methyl-3-penten-1-yne* (**13a**) and 16% *mesityl oxide* (**24a**), identical with authentic samples. The third fraction consisted of 55% *4-ethoxy-4-methyl-1,2-pentadiene* (**25a**). IR. spectrum in CCl_4 (cm^{-1}): 1950 (C=C=C), 1371, 1382 (gem. CH_3). NMR. spectrum in CCl_4 (ppm): 1.09 (*t*, 3 H), 1.21 (*s*, 6 H), 3.3 (*q*, 2 H), 4.8 (*m*, A_2B, 3 H).

$C_8H_{14}O$ (126.20) Calc. C 76.14 H 11.18% Found C 76.20 H 11.34%

cis- *and* trans-*3-Bromo-5-methyl-2,4-hexadienes* (**9**) *and* (**10**). 1.023 g (5.9 mmol) of a 1:1 mixture of isomers **9** and **10** in 59 ml of 80-vol.% ethanol (0.12 molar in triethylamine) were heated to 100° for 200 min. Gas-chromatography on column a) at 110° showed the presence of *2-methyl-2-hexen-4-yne* (**13b**) and *5-methyl-4-hexen-3-one* (**24b**), identical with authentic samples. The third fraction consisted of a 1:1 mixture of stereoisomeric *5-ethoxy-5-methyl-2,3-hexadienes* (**25b**). IR. spectrum in CCl_4 (cm^{-1}): 1658 (C=C=C), 1388, 1360 (gem. CH_3). NMR. spectrum in CCl_4 (ppm): 1.2 (*m*, 9 H), 1.67 (2*d*, 3 H), 3.30 (*q*, 2 H), 5.0 (*m*, 2 H).

$C_9H_{16}O$ (140.23) Calc. C 77.09 H 11.50% Found C 76.86 H 11.26%

Reaction of 68 mg (0.39 mmol) pure *cis*-isomer **9** in 3.9 ml 80% ethanol at 100° for 80 min led to 24% **13b**, 23% **24b** and 53% **25b**. From the pure *trans*-isomer **10**, 19% **13b**, 28% **24b** and 53% **25b** were obtained.

3-Bromo-2,5-dimethyl-2,4-hexadiene (**11**). 950 mg (5 mmol) **11** in 50 ml 80-vol.% ethanol (0.12 molar in triethylamine) were heated to 100° for 80 min. Gas-chromatography on column (a) showed the presence of pure *5-ethoxy-2,5-dimethyl-2,3-hexadiene* (**25c**). IR. spectrum in CCl_4 (cm^{-1}): 1960 (C=C=C), 1369, 1382 (gem. CH_3). NMR. spectrum in CCl_4 (ppm): 1.05 (*t*, 3 H), 1.15 (*s*, 6 H), 1.63, 1.68 (2*s*, 2 × 3 H), 3.28 (*q*, 2 H), 4.81 (*m*, 1 H).

$C_{10}H_{18}O$ (154.25) Calc. C 77.86 H 11.76% Found C 77.61 H 11.59%

Kinetic measurements. – The rates of compounds **8**, **9**, **10** and **11** were measured by the conductometric method described earlier [17]. A conductivity cell for reactions under pressure (*Metrohm*) was used. The cell was filled with approx. 20 ml of a 10^{-3} M solution in 80-vol.% ethanol [18] containing 1.2 or 4.8 equivalents of triethylamine and immersed in a water or oil thermostat, temperature deviation ± 0.05°. The reactions were followed approx. to 90% completion and the rate constants calculated by the method of *Rosevear* [19] with the aid of a computer (IBM 1620). The mean error was ± 4%.

The rates of compounds **5**, **6** and **7** were measured by the titrimetric method previously described [1], mean error ± 5%.

Elemental analyses were carried out by Mr. *E. Thommen*. The NMR. spectra were measured by Mr. *K. Aegerter*.

BIBLIOGRAPHY

[1] Part. I: *C.A.Grob & G.Cseh*, Helv. *47*, 194 (1964).

[2] *H.G.Richey & J.M.Richey* in 'Carbonium Ions', Vol. II, p.899, Eds. *G.A.Olah & P.von R. Schleyer*, Wiley-Interscience, New York 1970; *M.Hanack*, Accounts chem. Res. *3*, 209 (1970).

[3] *C.A.Grob & R.Spaar*, Tetrahedron Letters *1969*, 1439.

[4] *J.C.Traynard*, Bull. Soc. chim. France *1962*, 19.

[5] *H.Suhr*, 'Anwendung der kernmagnetischen Resonanz in der organischen Chemie', S.145, Springer Verlag 1965; *E.B.Whipple, J.H.Goldstein & L.Mandell*, J. Amer. chem. Soc. *82*, 3010 (1960).

[6] *A.F.Fainberg & S.Winstein*, J. Amer. chem. Soc. *78*, 2770 (1956).

[7] *S.Winstein, E.Grunwald & H.W.Jones*, J. Amer. chem. Soc. *73*, 2700 (1951).

[8] *R.H.DeWolfe & W.G.Young*, Chem. Reviews *56*, 753 (1956).

[9] *C.K.Ingold*, 'Structure and Mechnism in Organic Chemistry', p.70, Cornell University Press, Ithaca NY 1953.

[10] *H.C.Brown et al.*, J. Amer. chem. Soc. *79*, 1897 (1957).

[11] *R.Sustmann, J.E.Williams, M.J.S.Dewar, L.C.Allen & P.von R.Schleyer*, J. Amer. chem. Soc. *91*, 5350 (1969).

[12] *P.von R.Schleyer & C.W.Woodworth*, J. Amer. chem. Soc. *90*, 6528 (1968).

[13] *B.W.Nash, D.A.Thomas, W.K.Warburton & T.D.Williams*, J. chem. Soc. *1965*, 2983.

[14] *I.A.Favorskaya, E.M.Aurinen & Y.P.Artsybasheva*, Ž. obšč. Chim. *28*, 1785 (1958).

[15] Organic Syntheses, Coll. Vol. *4*, 746 (1963).

[16] *L.Condal-Bosch*, J. chem. Educat. *41*, A 235 (1964); *R.Kaiser*, 'Chromatographie in der Gasphase', Vol. IV, p.101, Hochschultaschenbücher Verlag 1969.

[17] *C.A.Grob, H.P.Fischer, H.Link & E.Renk*, Helv. *46*, 1190 (1963).

[18] *E.Grunwald & S.Winstein*, J. Amer. chem. Soc. *70*, 846 (1948).

[19] *W.E.Rosevear*, J. Amer. chem. Soc. *53*, 1651 (1931).