254. Mesomeric Vinyl Cations. Part III. Stereochemistry of Cations derived from 2-Bromo-1,3-dienes

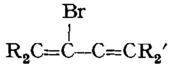
by **C. A. Grob** and **H. R. Pfaendler**

Institute of Organic Chemistry, University of Basel

(13. X. 70)

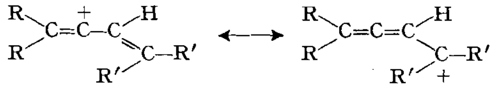
Summary. In contrast to their acyclic analogues, 2-bromocyclohexa-1,3-diene (**11a**) and 3-bromo-1,5-dimethyl-cyclohexa-1,3-diene (**11b**) do not react with silver ion, nor do they undergo solvolysis in 80% ethanol at temperatures up to 180°. The inertness to ionization of these cyclic bromodienes is attributed to steric inhibition of mesomerism involving the π electrons of the second double bond in the planar vinyl cation **12** and to the bent structure of this hypothetical intermediate.

As shown in Part II [1], the 4,4'-dimethyl derivative **1b** of 2-bromo-1,3-butadiene (**1a**) possesses remarkable solvolytic reactivity. In 80% ethanol it reacted more than 10^4 times as fast as the unsubstituted compound **1a**. On the other hand methyl substituents on C-1, as in **1c**, have little or no influence on the rate of ionization to the mesomeric vinyl cation **2a**↔**2b**. It was concluded, therefore, that charge delocalization, as implied by the limiting formula **2b**, is required to overcome the extreme inertness of vinyl halides to ionization.



$R_2C{=}\overset{\displaystyle Br}{\overset{|}{C}}{-}C{=}CR_2'$

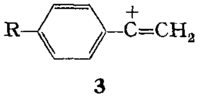
1



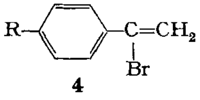
2a **2b**

a) $R = R' = H$ b) $R = H,\ R' = CH_3$ c) $R = R' = CH_3$

Charge delocalization, as in **2b**, requires that the planes of the double bonds in the bromodiene **1** intersect at an angle of approx. 90°. Furthermore, *sp*-hybridization of C-2 in the cation **2** demands an approximately linear arrangement of carbon atoms 1, 2 and 3. These stereochemical requirements were first postulated [2] for the aryl-vinyl cations **3** which are generated in the solvolysis of *p*-substituted α-bromostyrenes **4**[1]).



3



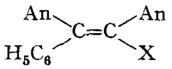
4

Recent literature reports tend to confirm this view. Thus acetolysis of *cis*- (**5a**) and *trans*-1,2-dianisyl-2-phenyl-vinyl bromides (**6a**) afforded a 1:1 mixture of the *cis*- and *trans*-acetates **5b** and **6b**, respectively, a result which suggests a linear *sp*-hybridized vinyl cation **7** as the product-determining intermediate [4]. The solvolysis products of the *cis*- and *trans*-forms of 1-cyclopropyl-1-iodo-propene (**8**) led to the

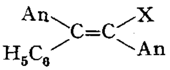
---

[1]) This topic has recently been reviewed [3].

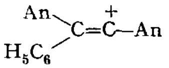
same conclusion, *i.e.* that a kinetically linear vinyl cation **9** is involved as an intermediate [5].



5



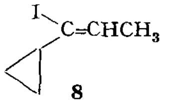
6



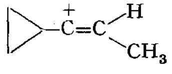
7

a) X = Br
b) X = OAc

An = p-$CH_3OC_6H_4$

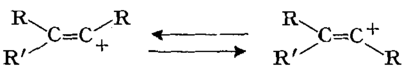


8



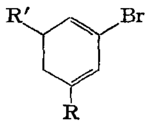
9

However, these results can be explained equally well by assuming a pair of rapidly interconverting 'bent' vinyl cations, **10a** and **10b**[2], as intermediates. Product studies of this kind cannot therefore be taken as evidence that a linear configuration represents an energy minimum, notwithstanding the fact that this view is supported by molecular orbital calculations [7].

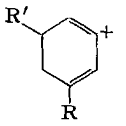


10a **10b**

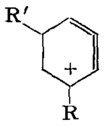
In order to elucidate the stereochemical aspects of mesomeric vinyl cations **2a** ↔ **2b** derived from 2-bromo-dienes **1**, a study of cyclic analogues, *i.e.* 2-bromo-1,3-cyclohexadiene (**11a**) and its dimethyl derivative **11b**, was undertaken. The diene system in the corresponding vinyl cations **12** is constrained to a non-linear geometry. Furthermore, its approximate planarity precludes assistance to ionisation of the bromine atom by the π electrons of the second double bond as symbolized by the limiting formula **13**. Very low solvolytic reactivity of the cyclic bromodienes **11a** and **11b** was therefore to be expected.



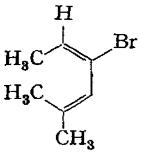
11



12



13



14

a) R = R′ = H b) R = R′ = CH_3 c) R = CH_3, R′ = H

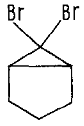
In selecting these models it was borne in mind that methyl substituents at C-4 of acyclic 2-bromodienes **1** markedly enhance solvolytic reactivity. 2-Bromo-1,3-cyclohexadiene (**11a**) corresponds to a 1,4-dialkyl substituted 2-bromodiene, a class of compounds which has been shown to possess only moderate reactivity [1]. 3-Bromo-1,5-dimethyl-cyclohexa-1,3-diene (**11b**), on the other hand, has the degree of alkyl substitution present in *cis*-3-bromo-5-methyl-2,4-hexadiene (**14**), which is one of

---

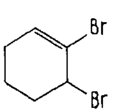
[2] Bent vinyl cations have been discussed as intermediates in the cyclisation of 6-heptyn-2-yl p-toluenesulfonate [6].

the most reactive 2-bromodienes studied to date [1]. In a stricter sense 3-bromo-1-methyl-1,3-cyclohexadiene (**11c**) is a more appropriate analogue of **14**. Due to its ready accessibility, however, the 1,5-dimethyl derivative **11b** was prepared, the assumption being made that a methyl group at C-5 would have little or no influence on reactivity.

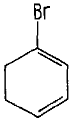
Syntheses. – *2-Bromocyclohexa-1,3-diene* (**11a**) has been prepared by thermal rearrangement of 6,6-dibromobicyclo[3.1.0]hexane (**15**) to 2,3-dibromocyclohexene (**16**) [8], followed by the elimination of HBr with quinoline [9]. The yields in both reactions were improved by careful temperature control in the first step and by substituting potassium *t*-butoxide for quinoline in the second step. Small amounts of the by-product 1-bromocyclohexa-1,3-diene (**17**) were separated by gas chromatography.



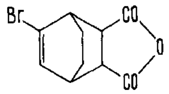
15



16



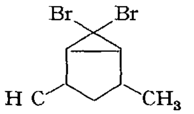
17



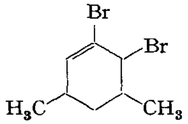
18

The structure of the cyclic bromodiene **11a** follows from its UV. spectrum (λ_{max}^{EtOH} 263 nm, $\varepsilon = 3000$) and from its *Diels-Alder* adduct **18** with maleic anhydride, the NMR. spectrum of which shows only one vinylic proton. **11a** rapidly resinifies when exposed to air at room temperature, but is stable at −20° under anaerobic conditions.

19



20



21

3-Bromo-1,5-dimethyl-cyclohexa-1,3-diene (**11b**) was synthesized from *cis*-3,5-dimethylcyclopentene (**19**)[3] by addition of dibromocarbene (from $CHBr_3$), yielding a mixture of *endo-* and *exo*-6,6-dibromo-*cis*-2,4-dimethyl-bicyclohexane (**20**). This mixture rearranged to 2,3-dibromo-*cis*-4,6-dimethyl-cyclohexene (**21**) upon heating to 130 °C/30 Torr. Because of its symmetry, the geminal dibromide **20** can afford only the vicinal dibromide **21**. Treatment of the latter with potassium *t*-butoxide afforded 3-bromo-1,5-dimethyl-cyclohexa-1,3-diene (**11b**) which showed the expected UV. absorption (λ_{max}^{EtOH} 267 nm, $\varepsilon = 4000$). This compound can arise from **21** either by a normal 1,2-elimination of HBr or by an *E*2′ process involving the hydrogen atom at C-6 and the C-3 bromine atom.

Results. – Whereas an immediate precipitate of silver bromide is obtained from the acyclic bromodiene **14** and ethanolic silver nitrate, no reaction occurs with the cyclic bromodienes **11a** and **11b**, even after one hour at 70°. Attempts to solvolyse the latter compounds in 80% aqueous ethanol by heating for 24 hours at 180° in sealed tubes were equally unsuccessful, only starting material being isolated.

The unreactivity of **11b** is remarkable and constrasts with the high reactivity of its acyclic analogue **14**, the half life of which is, in 80% ethanol, 25 min at 90° [1].

---

[3] The preparation of this compound is described in the following article [10].

This result confirms the conclusion that acyclic bromodienes derive their high solvolytic reactivity from delocalization of the positive charge in the intermediate linear vinyl cations **2a** ↔ **2b** [1]. A differentiation between the two factors which can contribute to the unreactivity of the cyclic analogue **11b**, *i.e.* planarity and nonlinearity of the 2-bromodiene system is, however, not possible on this basis.

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

Experimental Section

Melting points are corrected, boiling points uncorrected. The measurements of UV., IR. and NMR. spectra and the separations by gas chromatography were carried out as described in Part II [1].

2,3-Dibromocyclohexene (**16**). 60.0 g (0.25 mol) of 6,6-dibromobicyclo[3.1.0]hexane (**15**) [8] were heated under reflux at 23 Torr for 3 h in a heating bath kept at 125°[4]). After refluxing had subsided the bath temperature was raised to 140° for one h. The reaction product was then distilled at 11 Torr yielding 2.5 g of a forerun and 52 g (87%) of pure 2,3-dibromocyclohexene (**16**), b.p. 105–107°, n_D^{20} 1.576 (Lit. [8]: b.p. 105–106°/9 Torr, n_D^{25} 1.5764).

2-Bromocyclohexa-1,3-diene (**11a**). 12.0 g (0.05 mol) of 2,3-dibromocyclohexene (**16**) were stirred with 52 ml of a 1.0 M solution of potassium *t*-butoxide in abs. *t*-butanol under nitrogen for 15 h at 40°. 75 ml of pentane were then added. The mixture was extracted 5 times with water, the pentane layer separated, dried over $MgSO_4$ and evaporated to dryness under nitrogen. Distillation of the residue yielded 7.0 g (88%) of **11a**, b.p. 43–45°/11 Torr, contaminated with 10% of 1-bromocyclohexa-1,3-diene (**17**), as determined by gas chromatography.

C_6H_7Br (159.03) Calc. C 45.31 H 4.44% Found C 45.11 H 4.34%

Separation of a sample of the distillation by gas chromatography on a 6 m column (10% Carbowax on Chromosorb A AW) at 100° yielded pure 2-bromocyclohexa-1,3-diene (**11a**) which was stored under exclusion of air. UV. spectrum in ethanol λ_{max} 263 nm (ε = 2700). NMR. spectrum in CCl_4 (ppm): 2.2 (*d*, 4 H, *J* = 1.5), 5.8 (*m*, 2 H) and 6.0 (*m*, 1 H), –CH=, in agreement with literature values [9].

C_6H_7Br (159.03) Calc. C 45.31 H 4.44 Br 50.25% Found C 45.48 H 4.49 Br 50.21%

*Anhydride of 5-bromobicyclo[2.2.2]oct-5-ene-*endo*-2,3-dicarboxylic acid* (**18**). 320 mg (2 mmol) of 2-bromocyclohexa-1,3-diene (**11a**) and 200 mg (2 mmol) of maleic anhydride were heated in 2 ml toluene under reflux for 10 h. Upon cooling and addition of 5 ml CCl_4, 400 mg of crude **18** separated. After two recrystallizations from CCl_4 260 mg (51%) of platelets were obtained, m.p. 120°. NMR. spectrum in $CDCl_3$ (ppm): 1.6 (*d*, *J* = 1.5, 4 H), 3.2 (*m*, 2 H), 3.4 (*m*, 2 H), 6.4 (*d*, *J* = 7, 1 H, –CH=).

$C_{10}H_9BrO_3$ (255.07) Calc. C 47.08 H 2.77 Br 31.33% Found C 46.95 H 3.07 Br 31.20%

*6,6-Dibromo-*cis*-2,4-dimethyl-bicyclo[3.1.0.]hexane* (**20**). In a 250 ml threeneck flask, equipped with a stirrer, dropping funnel and reflux condenser closed by a drying tube, were placed 8.0 g (0.083 mol) of *cis*-3,5-dimethylcyclopentene (**19**) [10] and 25.3 g (0.1 mol) of bromoform. After cooling to – 5°, 100 ml of a 1 N solution of potassium *t*-butoxide in *t*-butanol were added dropwise with stirring over a 3 h period. After further stirring at 20° for 30 min., 150 ml of pentane were added. The mixture was then washed five times with 200 ml portions of water, the pentane layer dried over $MgSO_4$ and fractionally distilled. 2.0 g of unreacted **19** were separated at normal pressure. Further distillation at 11 Torr yielded 7.2 g forerun, b.p. 40–41°, and at 0.3 Torr 8.4 g (36%) of the dibromide **20**, b.p. 56–57°.

$C_8H_{12}Br_2$ (268.00) Calc. C 35.85 H 4.51 Br 59.64% Found C 36.03 H 4.47 Br 59.88%

---

[4]) It is important to maintain the vacuum throughout this exothermic reaction. Otherwise overheating may lead to explosions.

*2,3-Dibromo-*cis*-4,6-dimethyl-cyclohexene* (**21**). 7.0 g (26 mmol) **20** were heated under reflux at 30 Torr in an oil bath kept at 160°. The boiling point of the liquid rose within 3 h from 124° to 130°[4]). The product was heated for an additional hour to reflux and then fractionally distilled in a spinning band column at 0.3 Torr. The main fraction consisted of 3.9 g dibromide **21**, b.p. 67–68°; n_D^{20} 1.544. NMR. spectrum in CCl_4 (ppm): 1.0–1.3 (*m*, 6 H, CH_3), 1.3–2.6 (*m*, 4 H), 4.4 (*m*, 1 H, CHBr), 6.0 (*m*, 1 H, –CH=).

$C_8H_{12}Br_2$ (268.00) Calc. C 35.85 H 4.51 Br 59.64% Found C 35.94 H 4.50 Br 59.88%

3-Bromo-1,5-dimethyl-cyclohexa-1,3-diene (**11b**). 2.68 (10 mmol) **21** were heated with 15 ml of 1 M potassium *t*-butoxide in *t*-butanol under nitrogen at 45–50° for 7 h. The reaction mixture was diluted with 50 ml pentane and washed 5 times with 100 ml of water. The pentane layer was dried over $MgSO_4$ and evaporated to dryness. Distillation of the oily residue at 11 Torr yielded 1.4 g (75%) of **11b**, b.p. 75–77°, n_D^{20} 1.518. UV. spectrum in ethanol: λ_{max} 267 nm (ε = 4000). NMR. spectrum in CCl_4 (ppm): 1.05 (3 H, *d*, $J = 8$, CH_3), 1.8 (3 H, *s*, CH_3), 1.7–2.8 (3 H, *m*), 5.6 (2 H, *m*, –CH=).

$C_8H_{11}Br$ (187.09) Calc. C 51.36 H 5.93 Br 42.71% Found C 51.13 H 5.94 Br 42.98%

Solvolysis experiments. 0.01 M solutions of the bromodienes **11a** and **11b** in 80-vol.% ethanol, 0.012 M in triethylamine, were heated in sealed tubes at 180°. 5 ml aliquots were removed at regular intervals and acidified with 2 N HNO_3. No bromide was detectable with silver nitrate, even after a 24 h reaction.

0.1 M solutions of the bromodienes **11a** and **11b** in 80-vol.% ethanol, 0.12 M in triethylamine, were heated at 180° for 24 h. The solutions were diluted with water, acidified with HCl and continuously extracted with pentane in a *Kutscher-Steudel* extractor. The pentane extracts were dried over $MgSO_4$ and evaporated to dryness in a nitrogen atmosphere. Gas chromatography and spectral analysis showed the residues to consist of starting material containing only traces of impurities.

BIBLIOGRAPHY

[1] *C.A.Grob & R.Spaar*, Helv. *53*, 2119 (1970).
[2] *C.A.Grob & G.Cseh*, Helv. *47*, 194 (1964).
[3] *H.C.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).
[4] *Z.Rappoport & Y.Apeloig*, J. Amer. chem. Soc. *91*, 6734 (1969).
[5] *D.R.Kelsey & R.G.Bergman*, J. Amer. chem. Soc. *92*, 228 (1970).
[6] *P.E.Peterson & R.J.Kamat*, J. Amer. chem. Soc. *88*, 3152 (1966).
[7] *R.Sustmann, J.E.Williams, M.J.S.Dewar, L.C.Allen & P. von R.Schleyer*, J. Amer. chem. Soc. *91*, 5350 (1969).
[8] *J.Sonnenberg & S.Winstein*, J. org. Chemistry *27*, 748 (1962).
[9] *A.T.Bottini & W.Schear*, J. org. Chemistry *30*, 3205 (1965).
[10] *C.A.Grob & H.R.Pfaendler*, Helv. *53*, 2156 (1970).