Organohalogen Compounds. Part I. The Preparation of 1,4-Dibromo-2,3-dimethylbuta-1,3-diene and 1-Bromo-4-chloro-2,3-dimethylbuta-1,3-diene

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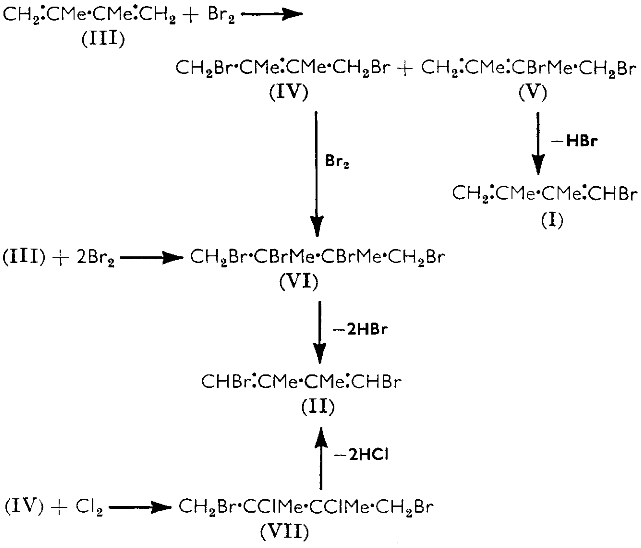
Dehydrobromination of 1,2,3,4-tetrabromo-2,3-dimethylbutane gives 1,4-dibromo-2,3-dimethylbuta-1,3-diene in high yield, but 3,4-dibromo-2,3-dimethylbut-1-ene does not dehydrobrominate to 1-bromo-2,3-dimethylbuta-1,3-diene. Chlorination of *trans*-1,4-dibromo-2,3-dimethylbut-2-ene gives a mixture of 1,3-dibromo-2,4-dichloro-2,3-dimethylbutane and a substitution product probably 4-bromo-3-chloro-2-chloromethyl-3-methylbut-1-ene; the former dehydrohalogenates to give either 4-bromo-1,3-dichloro-2,3-dimethylbut-1-ene or 1-bromo-4-chloro-2,3-dimethylbuta-1,3-diene depending on the reaction conditions.

As part of a study into the preparation and chemistry of halogeno-substituted buta-1,3-dienes the following routes to 1-bromo- and 1,4-dibromo-2,3-dimethylbuta-1,3-diene, (I) and (II), respectively, were investigated.

It has been observed previously [1] that the bromination of 2,3-dimethylbuta-1,3-diene (III) results in the formation of four of the five possible bromine adducts, *i.e.* *trans*-1,4-dibromo-2,3-dimethylbut-2-ene (IV), 3,4-dibromo-2,3-dimethylbut-1-ene (V), and *meso*- and (±)-1,2,3,4-tetrabromo-2,3-dimethylbutane (VI); the *cis*-1,4-dibromide was not detected. The relative amounts of the products can vary widely according to the experimental conditions employed, and allylic rearrangement of the dibromides (IV) and (V) to give mixtures containing mainly the thermodynamically more-stable isomer (IV) further complicates the reaction. An early literature report [2] on the liquid-phase bromination of diene (III) failed to evaluate the effect of allylic rearrangement.

Similarly, the reaction of bromine with buta-1,3-diene has been reported [3] not to give any *cis*-1,4-dibromide, but recently it has been observed that although this is correct for reaction at low concentration in solvent in light, reaction at higher concentration does afford some *cis*-1,4-dibromide by a radical mechanism.[4] Isoprene also forms *cis*-1,4-dibromide in addition to the other expected products on bromination.[5]



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[1] A. You-Lan Yao Ku, Ph.D. Thesis, University of Texas, 1962.

[2] E. H. Farmer, C. D. Lawrence, and W. D. Scott, *J. Chem. Soc.*, 1930, 510.

[3] L. F. Hatch, P. D. Gardner, and R. E. Gilbert, *J. Amer. Chem. Soc.*, 1959, **81**, 5943.

[4] V. L. Heasley and S. K. Taylor, *J. Org. Chem.*, 1969, **34**, 1779.

[5] V. L. Heasley, C. L. Frye, R. T. Gore, and P. S. Wilday, *J. Org. Chem.*, 1968, **33**, 2342.

In the present work it was found that bromination of the diene (III) at −78° in the dark using an equimolar ratio of reactants gave products the ratios of which did not vary greatly over the range of solvents (cyclopentane, methylene chloride, ether, and hexane) used; *i.e.* (IV) (64—71%), (V) (9—14%), (VI) (4—9%). The yields of these products are comparable to those reported[1] for the reaction at 10° in various solvents (hexane, chloroform, carbon tetrachloride, and carbon disulphide); (IV) (65—75%), (V) (19—27%), (VI) (6%). A higher yield (85%) of the *trans*-1,4-dibromide (IV) was obtained by reaction of equimolar amounts of reactants at 0° in methylene chloride.

Further bromination of the dibromide (IV) with an equimolar quantity of bromine in carbon tetrachloride gave a mixture (69%) of the *meso*- and (±)-tetrabromide (VI). Stereospecific *trans*-addition to the dibromide (IV) would have given only the *meso*-tetrabromide. Similarly bromination of the diene (III) using a 2 : 1 molar ratio of reactants in methylene chloride at −78° afforded a mixture (52%) of the two tetrabromides in a 4 : 1 ratio (n.m.r.), but it was not possible to determine unambiguously which isomer had which configuration. On the basis of melting points (major isomer, m.p. 124°; minor isomer, m.p. 137—138°), it is suggested that the former is the least symmetrical (±)-isomer and the latter the *meso*-isomer.

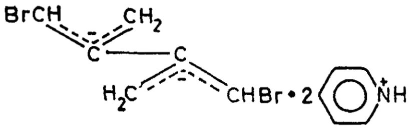
Attempted dehydrobromination of the 3,4-dibromide (V) to diene (I) with potassium hydroxide at atmospheric pressure gave only a rubber-like polymer.

Similarly reaction of the tetrabromide (VI) with potassium hydroxide at atmospheric pressure afforded only a solid polymer, but reaction at 80—110° *in vacuo* gave the diene (II) (89%), which was identified by elemental analysis, and mass (M^+; 44%), i.r. (strong bands at 6·20 and 6·35 μm, conj. C:C str.), and n.m.r. spectroscopy.

The ^{1}H n.m.r. spectrum showed the presence of two isomers in the ratio 3 : 1; major isomer bands at τ 8·05 (CH_3) and 3·65 (vinylic H), minor isomer bands at τ 8·00 (CH_3) and 3·53 (vinylic H), but the u.v. spectrum [absorption bands at $\lambda_{max.}$ (hexane) 239·5—240·5 nm and λ_{infl} 246—248 and 256—258 nm] indicated the presence of three isomers.

Attempted dehydrobromination of the tetrabromide (VI) with pyridine at 80° gave a dipyridinium salt (42%) [possible structure (VIII)], polymeric material and pyridine hydrobromide. Dehydrobromination at 30° afforded the salt (VIII) (16%), polymeric material, pyridine hydrobromide, and a liquid product which was shown (i.r. and n.m.r.) to contain the diene (II).

The salt (VIII) was soluble in water, insoluble in ether, chloroform, or carbon tetrachloride, and slightly soluble in alcohols (in which it slowly decomposed). Elemental analysis and a molecular-weight determination gave the molecular formula $C_8H_8Br_2,2C_5H_5N$. The salt was considered to have structure (VIII) and not to be a dipyridinium compound of formula $[C_5H_5\overset{+}{N}\cdot CH{:}CMe\cdot CMe{:}CH\cdot\overset{+}{N}C_5H_5]2Br^-$ because reaction with moist silver oxide gave pyridine and polymeric material and not the expected bis-quaternary ammonium hydroxide.



(VIII)

The salt (VIII) reacted with an excess of bromine in methanol at room temperature to afford a solid 3 : 1 adduct (90%), which was hygroscopic and regenerated salt (VIII) with the liberation of bromine when it was dissolved in methylene chloride or alcohols.

Reaction of the dibromide (IV) with chlorine in carbon tetrachloride at 0° gave two products, a solid 1 : 1 adduct $C_6H_{10}Cl_2Br_2$ (52%) and a liquid $C_6H_9ClBr_2$ (39%). There are three possible 1 : 1 adducts which could be formed in this reaction, 1,4-dibromo-2,3-dichloro-2,3-dimethylbutane (VII), 1,3-dibromo-2,4-dichloro-2,3-dimethylbutane (IX), and 1,2-dibromo-3,4-dichloro-2,3-dimethylbutane (X). The product was identified as having structure (IX) on the basis of the following evidence.

(i) Complete dehydrohalogenation (see later) afforded 1-bromo-4-chloro-2,3-dimethylbuta-1,3-diene (XI) (87%), which could only be formed from compounds (IX) or (X) and not from the expected adduct (VII) which would have given diene (II).

$CH_2Br\cdot CClMe\cdot CBrMe\cdot CH_2Cl$
(IX)

$CH_2Br\cdot CBrMe\cdot CClMe\cdot CH_2Cl$
(X)

$CHBr{:}CMe\cdot CMe{:}HCl$
(XI)

(ii) The mass spectrum of the adduct showed peaks at *m/e* 281, 279, 277, and 275 [15%, $(M - Cl)^+$], 237, 235, 233, and 231 [100%, $(M - Br)^+$], and 159, 157, and 155 (74%, $C_3H_5ClBr^+$). The latter ion would be expected in the spectrum of compound (IX) but not in that of compound (X). The spectra of the tetrahalides (VI) and 1,2,3,4-tetrachloro-2,3-dimethylbutane[6] show peaks at *m/e* 203, 201, and 199 (25%, $C_3H_5Br_2^+$) and 115, 113, and 111 (30%, $C_3H_5Cl_2^+$), respectively, and thus strong peaks due to these ions would be expected if the adduct had structure (X); the former was not observed and the latter was only of relatively low intensity. The possibility that the ion $C_3H_5BrCl^+$ arose by rearrangement was discounted because the spectrum of 2,3-dibromo-1,4-dichloro-2,3-dimethylbutane,[6] which showed a similar breakdown pattern to that of compound (IX), contained strong peaks assigned to the ion $C_3H_5BrCl^+$ but not peaks due to the rearrangement ions $C_3H_5Cl_2^+$ or $C_3H_5Br_2^+$.

The ^{1}H n.m.r. spectrum was as expected for a non-symmetrical 1,2,3,4-tetrahalogeno-2,3-dimethylbutane

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[6] Miss E. Z. Said and A. E. Tipping, unpublished results.

and showed the presence of one (±)-pair only, but it did not differentiate between structures (IX) and (X).

The liquid product $C_6H_9Br_2Cl$ was shown by i.r. (band at 5·41 μm) and n.m.r. spectroscopy (two non-equivalent vinylic protons at τ 4·38 and 4·50) to contain a $CH_2{:}C$ group. The product could therefore be 3,4-dibromo-2-chloromethyl-3-methylbut-1-ene (XII), 4-bromo-2-bromomethyl-3-chloro-3-methylbut-1-ene (XIII), or 3-bromo-2-bromomethyl-4-chloro-3-methylbut-1-ene (XIV).

$CH_2{:}C(CH_2Cl){\cdot}CBrMe{\cdot}CH_2Br$
(XII)

$CH_2{:}C(CH_2Br){\cdot}CClMe{\cdot}CH_2Br$
(XIII)

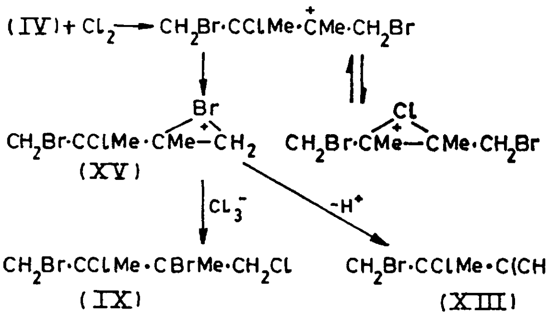
$CH_2{:}C(CH_2Br){\cdot}CBrMe{\cdot}CH_2Cl$
(XIV)

The geminal coupling (J 10·8 Hz) observed in the n.m.r. spectrum for the non-allylic CH_2X group is closer in magnitude to that for a CH_2Br group, *e.g.* $CHCl{:}CMe{\cdot}CClMe{\cdot}CH_2Br$ (J 10·5 Hz), than for a CH_2Cl group (11·5—12·5 Hz) in other compounds prepared in the present work. It has been previously reported [7] that geminal couplings for CH_2Br groups are smaller than those for CH_2Cl groups in similar compounds, *e.g.* $CH_2Br{\cdot}CHBrMe$ (J 9·8 Hz), $CH_2Cl{\cdot}CHClMe$ (J 11·1 Hz).

It is therefore considered more probable that the compound has structure (XII) or (XIII) rather than (XIV).

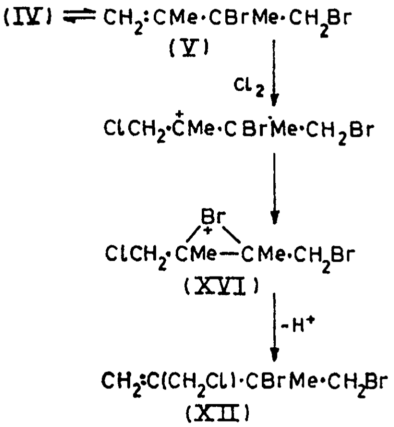
The observation that the compound did not undergo ready allylic rearrangement when stored in contrast to 3,4-dibromo-2,3-dimethylbut-1-ene [which rearranges to the *trans*-1,4-dibromide (IV)] is perhaps evidence in favour of the presence of a 3-chloro-substituent, as in compound (XIII), rather than a 3-bromo-substituent, as in compound (XII).

The saturated compound (IX) and the olefin (XIII) could be formed *via* a common intermediate (XV).



Since bromine is more efficient at neighbouring group participation than is chlorine, attack by chlorine on the olefin (IV) would be expected to result in formation of the cyclic bromonium ion intermediate (XV). This intermediate can then undergo reaction with Cl_3^- ion at the less hindered CH_2 group to form (IX) or can lose a methyl proton to afford (XIII).

The olefin (XII) is possibly best explained as being formed *via* isomerisation of the dibromide (IV) to (V). However, it is surprising that if this mechanism is correct that proton loss from the intermediate (XVI) is so specific and that a mixture of the olefins (XII) and (XIV) do not result. Furthermore attack on the intermediate (XVI) by Cl_3^- ion would be expected and



since the tetrahalide (IX) is the only tetrahalide isolated this must occur exclusively at the $CMe{\cdot}CH_2Br$ group.

It is difficult to explain why reaction of the intermediate (XVI) should be so specific and on balance it is more probable that the intermediate (XV) is involved and that the olefinic product has structure (XIII).

Dehydrobromination of the tetrahalide (IX) with potassium hydroxide at 110° *in vacuo* gave the diene (XI) which was identified on the basis of elemental analysis and spectroscopic evidence. The mass spectrum showed a molecular ion at m/e 198, 196, and 194 (68%) and base peaks at m/e 117 and 115 $(M - Br)^+$ and absorptions observed in the i.r. (at 6·18 and 6·33 μm) and u.v. spectra (at $\lambda_{max.}$ 239—240 and 246 nm and λ_{infl} 253—255 nm) were characteristic of a conjugated diene. Although the u.v. spectrum indicated the presence of three isomers, *cf.* the diene (II), the n.m.r. spectrum, a complex ABX_3Y_3 system, only indicated the presence of one isomer.

Partial dehydrohalogenation of the tetrahalide (IX) took place on reaction with potassium hydroxide at 85° *in vacuo* to afford 4-bromo-1,3-dichloro-2,3-dimethylbut-1-ene (XVII) (67%).

$$CH_2Cl{\cdot}CBrMe{\cdot}CClMe{\cdot}CH_2Br \xrightarrow{KOH} CHCl{:}CMe{\cdot}CClMe{\cdot}CH_2Br$$
(XVII)

This indicates that the diene (XI) is formed *via* initial dehydrobromination to give the olefin (XVII) followed by dehydrochlorination.

EXPERIMENTAL

2,3-Dimethylbutadiene was prepared in 30% overall yield from acetone. Solvents were carefully dried, distilled, and their purity checked (i.r., g.l.c.) before use. Products were separated either by fractionation at atmospheric or

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[7] H. Finegold, *Proc. Chem. Soc.*, 1962, 213.

reduced pressure or by liquid-phase chromatography [activated alumina Type H, 100—200 mesh; elution solvents, light petroleum followed by chloroform (unless stated to the contrary)]. The identities of products were established by elemental analysis, i.r. spectroscopy (Perkin-Elmer spectrophotometer model 257 with sodium chloride optics), ^1H n.m.r. spectroscopy (Perkin-Elmer R10 or Varian HA100 instruments operating at 60·0 and 100·0 MHz, respectively, with tetramethylsilane as internal reference), mass spectrometry (A.E.I. MS 902 spectrometer), and u.v. spectroscopy (Unicam SP 700 spectrophotometer using hexane as solvent).

Reaction of 2,3-*Dimethylbuta*-1,3-*diene with Bromine*.—(a) *Cyclopentane solvent.* A solution of bromine (40·0 g, 0·25 mol) in cyclopentane (80 ml) was added dropwise (90 min) to a well-stirred solution of the diene (20·0 g, 0·24 mol) in cyclopentane (100 ml) at −78°. The solvent was removed under reduced pressure, the reaction mixture was then cooled, and the resultant precipitate (43·5 g) was removed by filtration. Treatment of the precipitate with cold ethanol gave (i) a mixture of *meso*- and (±)-1,2,3,4-tetrabromo-2,3-dimethylbutane (4·10 g, 10·2 mmol, 6%) (Found: C, 17·9; H, 2·4; Br, 79·4. Calc. for $C_6H_{10}Br_4$: C, 17·8; H, 2·5; Br, 79·5%), m.p. (from ether) 138—139° (lit.,[8] m.p. 138—139°); *m/e* 325, 323, 321, and 319 [100%, $(M-Br)^+$], 243, 241, and 239 [39%, $(M-HBr_2)^+$], and 203, 201, and 199 (25%, $C_3H_5Br_2^+$); ^1H n.m.r. spectrum (saturated solution in benzene) showed the presence of two isomers with bands for isomer 1 at τ 6·12 (d, 2H, H_a in CH_2Br groups, J_{a-b} 11·5 Hz), 6·35 (dq, 2H, H_b in CH_2Br groups, J_{b-Me} 0·8 Hz), and 8·30 (d, 6H, 2Me) and bands for isomer 2 at 6·28 (d, 2H, H_a, J_{a-b} 11·5 Hz), 6·50 (dq, 2H, H_b, J_{b-Me} 0·7 Hz), and 8·24 (d, 6H, 2Me); (ii) an ethanolic solution, which on removal of the solvent gave *trans*-1,4-dibromo-2,3-dimethylbut-2-ene (37·0 g, 0·15 mol, 71%) (Found: C, 29·8; H, 3·9; Br, 66·0. Calc. for $C_6H_{10}Br_2$: C, 29·8; H, 4·1; Br, 66·0), m.p. (hexane) 45—46° (lit.,[8] m.p. 46°); ^1H n.m.r. bands at τ 6·02 (s, 4H, $2CH_2Br$) and 8·10 (s, 6H, 2Me).

Distillation of the original liquid product afforded (i) unchanged diene (2·50 g, 30·5 mmol, 12% recovered), (ii) 3,4-dibromo-2,3-dimethylbut-1-ene (6·30 g, 26·3 mmol, 12%), b.p. 105—106°/25 mm (lit.,[8] b.p. 77·5—79·5°/5 mm); and (iii) a black residue (4·20 g). The i.r. spectra of all the bromine adducts were identical to those reported.[1]

(b) *Methylene chloride solvent.* Dropwise addition (90 min) of a solution of bromine (40·0 g, 0·25 mol) in methylene chloride (75 ml) to a well-stirred solution of the diene (20·0 g, 0·24 mol) in methylene chloride (150 ml) at −78° and work-up of the product as in experiment (a) gave (i) unchanged diene (3·15 g, 38·4 mmol, 16% recovered); (ii) *trans*-1,4-dibromide (34·2 g, 0·14 mol, 69%); (iii) 3,4-dibromide (5·60 g, 23·1 mmol, 11%); (iv) a mixture of *meso*- and (±)-tetrabromides (5·80 g, 14·4 mmol, 7%); and (v) a black residue (4·3 g).

(c) *Hexane solvent.* Reaction, as in experiment (a), of a solution of bromine (41·0 g, 0·26 mol) in hexane (100 ml) with a solution of the diene (20·5 g, 0·25 mol) in hexane (100 ml) at −78° gave (i) unchanged diene (2·50 g, 30·5 mmol, 12% recovered); (ii) *trans*-1,4-dibromide (34·4 g, 0·14 mol, 64%); (iii) 3,4-dibromide (7·3 g, 30·2 mmol, 14%); (iv) a mixture of *meso*- and (±)-tetrabromide (3·8 g, 9·4 mmol, 4%); and (v) a black residue (6·5 g).

(d) *Diethyl ether solvent.* Reaction, as in experiment (a), of a solution of bromine (37·3 g, 0·23 mol) in ether (75 ml) with a solution of the diene (18·5 g, 0·22 mol) in ether (100 ml) at −78° gave (i) unchanged diene (2·8 g, 34·1 mmol, 15% recovered); (ii) *trans*-1,4-dibromide (29·1 g, 0·12 mol, 65%); (iii) 3,4-dibromide (4·2 g, 17·3 mmol, 9%); (iv) a mixture of *meso*- and (±)-tetrabromide (6·5 g, 16·1 mmol, 9%); and (v) a black residue (3·5 g).

Preparation of 1,2,3,4-*Tetrabromo*-2,3-*dimethylbutane*.—A solution of bromine (40·0 g, 0·25 mol) in methylene chloride (50 ml) was added dropwise (90 min) to a stirred solution of 2,3-dimethylbuta-1,3-diene (10·0 g, 0·12 mol) in methylene chloride (1000 ml) at −78°; the stirring was continued (2 h). The solvent was removed under reduced pressure and the resultant solid was filtered and washed with ethanol to afford a mixture of *meso*- and (±)-1,2,3,4-tetrabromo-2,3-dimethylbutane (23·5 g, 62·9 mmol, 52%).

Preparation of trans-1,4-*Dibromo*-2,3-*dimethylbut*-2-*ene*.—A dilute solution of bromine (40·4 g, 0·25 mol) in methylene chloride (250 ml) was added dropwise (7 h) to a well-stirred solution of 2,3-dimethylbuta-1,3-diene (21·6 g, 0·26 mol) in methylene chloride (300 ml) at 0°. Removal of the solvent under reduced pressure gave a semi-solid residue (62·0 g) which was filtered to afford solid *trans*-1,4-dibromo-2,3-dimethylbut-2-ene (51·4 g, 0·21 mol, 85%). When stored the olefin was slowly converted into a mixture of the *trans*-1,4- and 3,4-dibromides (ratio *ca.* 85 : 15).

Reactions of trans-1,4-*Dibromo*-2,3-*dimethylbut*-2-*ene*.—(a) *With bromine.* A solution of bromine (6·7 g, 41·8 mmol) in carbon tetrachloride (25 ml) was added slowly (1 h) to a well-stirred solution of the dibromide (10·0 g, 41·3 mmol) in carbon tetrachloride (50 ml) at 0°. The resultant mixture was heated at 35—40° (15 min) and then cooled; the solid product was filtered off and washed with light petroleum to afford a mixture of *meso*- and (±)-1,2,3,4-tetrabromo-2,3-dimethylbutane (11·5 g, 28·6 mmol, 69%).

(b) *With iodine.* A mixture of the dibromide (10·6 g, 43·8 mmol) and iodine (11·4 g, 44·8 mmol) in methylene chloride (100 ml) was refluxed (1 h). Removal of the solvent under reduced pressure gave a dark solid, which on recrystallisation from light petroleum in the presence of charcoal afforded unchanged dibromide (4·0 g, 16·5 mmol, 37% recovered) and a dark solution containing polymeric material.

(c) *With chlorine.* Chlorine gas was bubbled slowly into a well-stirred solution of the dibromide (24·3 g, 77·6 mmol) in carbon tetrachloride (250 ml) at 0° until a chlorine colour persisted in the solution (3 h). Removal of the solvent under reduced pressure gave a mixture (25·8 g) of solid and liquid product. The solid was filtered off to give colourless crystals of 1,3-*dibromo*-2,4-*dichloro*-2,3-*dimethylbutane* (12·7 g, 40·6 mmol, 52%) (Found: C, 23·3; H, 3·2; total halogen, 63·4. $C_6H_{10}Br_2Cl_2$ requires C, 23·0; H, 3·2; total halogen, 63·8%), m.p. (light petrol) 111—112°; main i.r. bands at 6·88s, 6·95s, 7·08s, 7·28vs, 7·75s, 7·95s, 8·25s, 8·90s, 9·25s, 9·80vs, 11·35vs, 11·60s, 13·30vs, and 14·53vs μm; ^1H n.m.r. bands for $CH_aH_cBr\cdot CClMe_f\cdot$-$CBrMe_e\cdot CH_bH_dCl$ at τ 5·82 (d, H_a, J_{c-a} 11·5 Hz), 5·86 (d, H_b, J_{b-d} 12·0 Hz), 6·06 (dq, H_c, J_{f-c} 0·7 Hz), 6·07 (dq, H_d, J_{e-d} 0·4 Hz), 8·00 (d, 3H, Me_e), and 8·08 (d, 3H, Me_f).

Distillation of the filtrate under reduced pressure afforded a dark residue and a compound tentatively identified as 4-*bromo*-3-*chloro*-2-*bromomethyl*-3-*methylbut*-1-*ene* (8·40 g, 30·7 mmol, 39%) [Found: C, 25·8; H, 3·3;

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[8] O. J. Sweeting and J. R. Johnson, *J. Amer. Chem. Soc.*, 1946, **68**, 1057.

Br, 57·1; Cl, 12·2%; *M* (mass spectrometry), 276·5. $C_6H_9Br_2Cl$ requires C, 26·0; H, 3·3; Br, 57·9; Cl, 12·8%; *M*, 276·5], b.p. 65—68°/0·03 mm; i.r. bands at 3·25s, and 3·50m (C–H str.), 5·41s (CH_2:C), and 6·12m (C:C str.) μm; $\lambda_{max.}$ 213—214 nm (ε 2420); *m/e* 280, 278, 276, and 274 (5%, M^+), 243, 241, and 239 [19%, $(M - Cl)^+$], 199, 197, and 195 [100%, $(M - Br)^+$], 161, and 159 (20%, $C_6H_8Br^+$), and 117 and 115 (61%, $C_6H_8Cl^+$); ^1H n.m.r. bands for CH_aH_b:C(CH_2Br)·CClMe·CH_cH_dBr at τ 4·38 (t, H_a, J_{CH_2-a} 1·0 Hz), 4·50 (s, H_b), 5·88 (d, CH_2Cl), 6·12 (dq, H_c, J_{c-d} 10·8, J_{Me-c} 0·7 Hz), 6·31 (d, H_d), and 8·06 (d, Me).

Reactions of 1,2,3,4-*Tetrabromo*-2,3-*dimethylbutane*.—(a) *With potassium hydroxide.* The tetrabromide (3·2 g, 7·9 mmol) and dry, powdered potassium hydroxide (3·1 g) were heated together *in vacuo* at 100° (5 h) and the product was dried (molecular sieve type 4a, 8—12 mesh) and identified as 1,4-*dibromo*-2,3-*dimethylbuta*-1,3-*diene* (1·7 g, 7·1 mmol, 89%) [Found: C, 29·9; H, 3·4; Br, 66·9%; *M* (mass spectrometry), 240. $C_6H_8Br_2$ requires C, 30·0; H, 3·3; Br, 66·7%; *M*, 240].

(b) *With pyridine.* The tetrabromide (2·8 g, 6·9 mmol) was treated with an excess of dry pyridine (10·0 g, 0·11 mol) in the presence of hydroquinone (0·1 g) at 80° with continuous stirring (1 h). The resultant dark green solution was filtered to give a dark green filtrate (3·5 g) and a pale green residue. The filtrate was separated by liquid-phase chromatography to afford an unidentified deep green dense liquid (1·8 g) with main i.r. bands at 3·38s, 3·42vs, 6·16s, 7·92vs, 9·15s, 9·80s, and 12·50vs μm. The residue was washed with ether and then with ethanol (to remove pyridine hydrobromide) to give pale green crystals of a *dipyridinium salt* of 1,4-*dibromo*-2,3-*dimethylbuta*-1,3-*diene* (1·20 g, 2·90 mmol, 42%) (Found: C, 48·0; H, 4·7; N, 7·0; Br, 40·4. $C_{16}H_{18}N_2Br_2$ requires C, 48·2; H, 4·6; N, 7·0; Br, 40·2%), m.p. 233—235° (with decomp.), main i.r. bands at 3·26m and 3·45m (C–H str.); 6·18s, 6·66s, 6·78vs, 7·18s, 8·70s, 12·90s, and 14·50s μm; $\lambda_{max.}$ (ethanol) at 210—212 (ε 18,700) and 260 (ε 8750) nm and λ_{infl} 255 (ε 8150), 266—268 (ε 6660), 320—326 (ε 230) and 353—368 (ε 130) nm. The salt was soluble in water, slightly soluble in methanol, ethanol, dimethyl sulphoxide, or dimethylformamide (decomposition was apparent in these solvents after *ca.* 2 h at 20°), and insoluble in ether or carbon tetrachloride. It reacted with moist silver oxide at room temperature (2 h) with the formation of pyridine and a dark red polymeric liquid.

A second experiment carried out at 30° (5 days) gave the dipyridinium salt (16%) and a dense red liquid which was shown by i.r. and n.m.r. spectroscopy to contain 1,4-dibromo-2,3-dimethylbuta-1,3-diene.

Reaction of the Dipyridinium Salt with Bromine.—A solution of the salt (0·35 g, 0·88 mmol) in dry methanol (50 ml), treated with an excess of bromine (2·0 g, 12·3 mmol), gave a yellow solid (0·70 g, 0·80 mmol, 90%) (Found: C, 23·2; H, 2·5; N, 3·3; Br, 72·3. Calc. for $C_{16}H_{18}Br_8N_2$: C, 22·0; H, 2·1; N, 3·2; Br, 72·9%), m.p. 160°; main i.r. bands at 3·20w, 3·25w, 3·28w, and 3·30w (C–H str.), 6·74vs, 6·78s, 8·56s, 8·65s, 8·70s, 13·00s, and 14·70s μm; $\lambda_{max.}$ (ethanol) 208·5—209·5 (ε 24,150) and 260·5 (ε 9870) nm and λ_{infl} 360—375 (ε 75) nm. The salt was hygroscopic and slowly liberated bromine when dissolved in various solvents (*e.g.* methylene chloride, methanol, ethanol) to regenerate the dipyridinium salt.

Reaction of 1,4-*Dibromo*-2,3-*dimethylbuta*-1,3-*diene with Bromine.*—A solution of the diene (0·35 g, 1·50 mmol) in carbon tetrachloride (10 ml) in the presence of hydroquinone (trace) when refluxed (1 h) with a solution of bromine (1·0 g, 6·2 mmol) in carbon tetrachloride (20 ml), gave, after removal of the solvent under reduced pressure, a yellow dense polymeric liquid (0·20 g).

Attempted Dehydrobromination of 3,4-*Dibromo*-2,3-*dimethylbut*-1-*ene*.—The olefin (5·0 g, 20·6 mmol) was treated with an excess of powdered potassium hydroxide (20 g) at room temperature (6 days). The resultant material was treated with an excess of water and then extracted with ether (3 × 30 ml) to afford a yellow rubbery polymer (1·7 g) and an ethereal extract, which on removal of the solvent under reduced pressure gave a mixture of *trans*-1,4- and unchanged 3,4-dibromide (3·2 g, 13·2 mmol, 64%).

Reaction of 1,3-*Dibromo*-2,4-*dichloro*-2,3-*dimethylbutane with Potassium Hydroxide.*—(a) *At* 85°. The tetrahalide (3·0 g, 9·6 mmol), mixed with an excess of dry, powdered potassium hydroxide (5·0 g), was heated slowly *in vacuo* at 85° (5 h) to afford product which was dried (molecular sieve type 4A, 8—12 mesh) and identified as 4-*bromo*-1,3-*dichloro*-2,3-*dimethylbut*-1-*ene* (1·5 g, 6·4 mmol, 67%) (Found: C, 31·3; H, 3·9; $C_9H_9BrCl_2$ requires C, 31·1; H, 3·9%); i.r. bands at 3·22m, 3·35s, and 3·42s (C–H str.), and 6·20s (C:C str.) μm; *m/e* 236, 234, 232, and 230 (38%, M^+), 199, 197, and 195 [89%, $(M - Cl)^+$], 198, 196, and 194 [83%, $(M-HCl)^+$], 118 and 116 (40%, $C_6H_9Cl^+$), and 117 and 115 (100%, $C_6H_8Cl^+$); ^1H n.m.r. bands for CH_a-Cl:CMe_d·$CClMe_e$·CH_bH_cBr (20% solution in CCl_4) at τ 3·75 (q, 1H, H_a, J_{d-a} 1·5 Hz), 6·21 (dq, 1H, H_b, J_{c-b} 10·5 and J_{e-b} 0·7 Hz), 6·42 (d, 1H, H_c), 8·05 (d, 3H, H_d), and 8·12 (d, 3H, H_e).

The reaction residue was extracted with chloroform (3 × 25 ml) to give a dark polymeric material (0·6 g).

(b) *At* 110°. The tetrahalide (3·67 g, 11·72 mmol) and an excess of dry, powdered potassium hydroxide (14·5 g) were slowly heated *in vacuo* to 110° (2·5 h) to afford product which was dried as in (a) and identified as 1-*bromo*-4-*chloro*-2,3-*dimethylbuta*-1,3-*diene* (2·0 g, 10·23 mmol, 87%) [Found: C, 36·5; H, 4·2; total halogen 59·3%; *M* (mass spectrometry), 195·5. C_6H_8BrCl requires C, 36·8; H, 4·1; total halogen, 59·1%; *M*, 195·5], i.r. bands at 3·22s and 3·38s (C–H str.), and 6·18s and 6·33s (conj. C:C str.) μm; $\lambda_{max.}$ 239—240 (ε 7440) and 246 (ε 7540) nm and λ_{infl} 253—255 (ε 5345) nm; *m/e* 198, 196, and 194 (68%, M^+), 161 and 159 [15%, $(M - Cl^+)$], 117 and 115 [100%, $(M - Br)^+$], 79 (81%, $C_6H_7^+$), and 77 (60%, $C_6H_5^+$); ^1H n.m.r. bands at τ 3·58 (complex, 1H, CHBr), 3·70 (complex, 1H, CHCl), and 8·07 (complex, 6H, 2 × Me).

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