

Organohalogen Compounds, Part 3.¹ The Preparation and Certain Reactions of Chloro-substituted 2,3-dimethylbuta-1,3-dienes

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Summary: The dienes $\text{CH}_2=\text{C}(\text{CH}_2\text{Cl})\text{CMe}=\text{CH}_2$ (3), $\text{CHCl}=\text{CMe}\cdot\text{CMe}=\text{CH}_2$ (4), $\text{CHCl}=\text{CMe}\cdot\text{CMe}=\text{CHCl}$ (14), and $\text{CHCl}=\text{C}(\text{CH}_2\text{Cl})\cdot\text{CMe}=\text{CH}_2$ (21) have been synthesised via chlorination of 2,3-dimethylbuta-1,3-diene. Copper-catalysed addition of benzenesulphonyl chloride to 2,3-dimethylbuta-1,3-diene and diene (3) gives the 1,4-adducts $\text{PhSO}_2\cdot\text{CH}_2\cdot\text{CMe}=\text{CMe}\cdot\text{CH}_2\text{Cl}$ and a mixture of $\text{PhSO}_2\cdot\text{CH}_2\cdot\text{C}(\text{CH}_2\text{Cl})\cdot\text{CMe}\cdot\text{CH}_2\text{Cl}$ and $\text{PhSO}_2\cdot\text{CH}_2\cdot\text{CMe}=\text{C}(\text{CH}_2\text{Cl})_2$, respectively. Dehydrochlorination of the former adduct gives the diene $\text{PhSO}_2\text{CH}=\text{CMe}\cdot\text{CMe}=\text{CH}_2$ which polymerises in air. Dienes (4) and (21) form Diels-Alder adducts with tetracyanoethylene.

Chlorination of diene (14), is surprisingly accompanied by addition of hydrogen chloride and gives the compounds $\text{CHCl}_2\cdot\text{CClMe}\cdot\text{CClMe}\cdot\text{CH}_2\text{Cl}$ and $\text{CHCl}_2\cdot\text{CCl}(\text{CH}_2\text{Cl})\cdot\text{CClMe}\cdot\text{CH}_2\text{Cl}$. The dichloride $\text{CH}_2\text{Cl}\cdot\text{CMe}=\text{CMe}\cdot\text{CH}_2\text{Cl}$ reacts with an equimolar amount of bromine by addition, but with an excess of bromine the products are $\text{CH}_2\text{Br}\cdot\text{C}(\text{CH}_2\text{Cl})=\text{C}(\text{CH}_2\text{Cl})\cdot\text{CH}_2\text{Br}$ (89%) and $(\text{CH}_2\text{Br})_2\text{C}=\text{C}(\text{CH}_2\text{Cl})\cdot\text{CH}_2\text{Br}$ (6%). Unexpected substitutive bromination is observed on treatment of the trichloride $(\text{CH}_2\text{Cl})_2\text{C}=\text{CMe}\cdot\text{CH}_2\text{Cl}$ with bromine to give $(\text{CH}_2\text{Cl})_2\text{C}=\text{C}(\text{CH}_2\text{Cl})\cdot\text{CH}_2\text{Br}$ (95%).

Introduction

Although the chlorination of 2,3-dimethylbuta-1,3-diene (1) was reported [2] originally to give (*E*)-1,4-dichloro-2,3-dimethylbut-2-ene (2) as the only identified product. More recent work in this department has shown that a variety of products are formed [1].

Further investigation of the chlorination of diene (1) has been carried out to obtain precursors to various chloro-1,3'-dienes. The dienes were then prepared and certain of their reactions were investigated.

Chlorination of Diene (1)

Further products were isolated and identified from the chlorination and the results obtained are compared (Table 1) with those reported previously.

In experiment 2 the products were worked up immediately after the addition of chlorine was completed. This could account for the detection and isolation of the kinetically favoured 1,2-dichloride (5), since it would be expected to rearrange to a

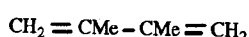
Table 1: Chlorination of diene (1) at -20°C with a solution of chlorine in carbontetrachloride (2H)

Experiment	Recovered (1) (%)	(3)	(4)	(5)	Products (%)	(6) ⁺	(7)	(8)
1 ^a	67	51	1		47			
2 ^b	43	16		5	48	trace	5.5	10

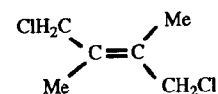
^aIn order of increasing g.l.c. retention time. ⁺ Tentatively identified on the basis of an almost identical mass spectrum to that of compound (7).

^bprevious work [1]

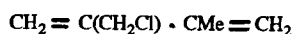
present work



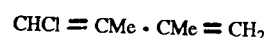
(1)



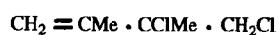
(2)



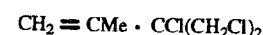
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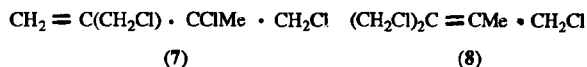


(5)



(6)

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large extent on storage to the thermodynamically favoured 1,4-dichloride (2) especially in the presence of hydrogen chloride formed by substitutive chlorination. Dichloride (5) has been prepared previously by treatment of diene (1) with iodobenzene dichloride [3].

The yields of dichloride (2) from the two experiments were the same, but the yield of monochloride (3) was much lower in experiment 2 which indicated that it was probably the main precursor to the trichlorides (6), (7), and (8) as shown in Scheme 1.

However, dichloride (2) could also have reacted further to give the trichlorides and so its chlorination in CH_2Cl_2 at room temperature was investigated. This gave trichloride (7) (84%), com-

tilation of the reaction mixture at reduced pressure gave unchanged (2) (4% recovered), (6) (7%) (10%), (8), (60%) and (9) (10%) which showed that the initial major product (7) had undergone thermal isomerisation to (8). This ready thermal isomerisation was confirmed in a separate experiment and the equilibrium ratio [(8): (9)] was found to be 98:2 at 105°C.

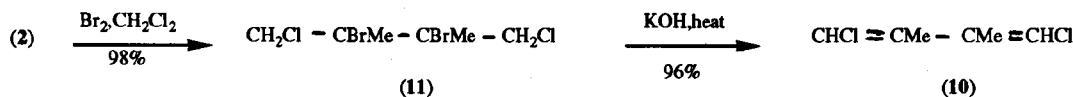
Compounds (7) and (9) are probably formed as shown in Scheme 2.

Preparation of chlorinated 1,3-Dienes

(a) 1,4-Dichloro-2,3-dimethylbuta-1,3-diene (10).

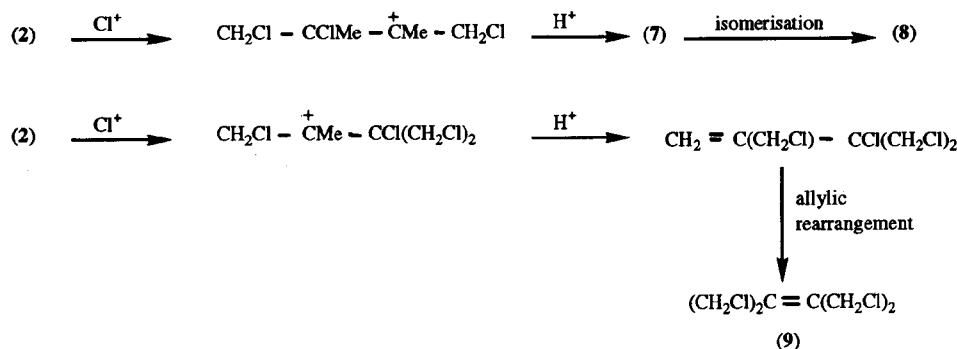
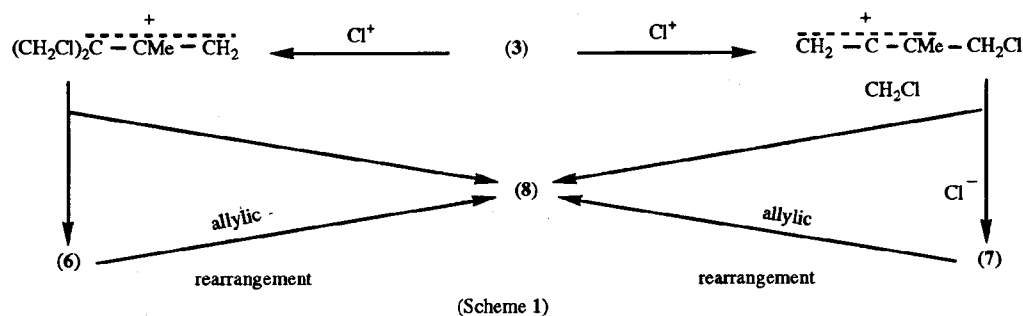
The diene has been prepared previously by the route shown [equation (E1)] [1].

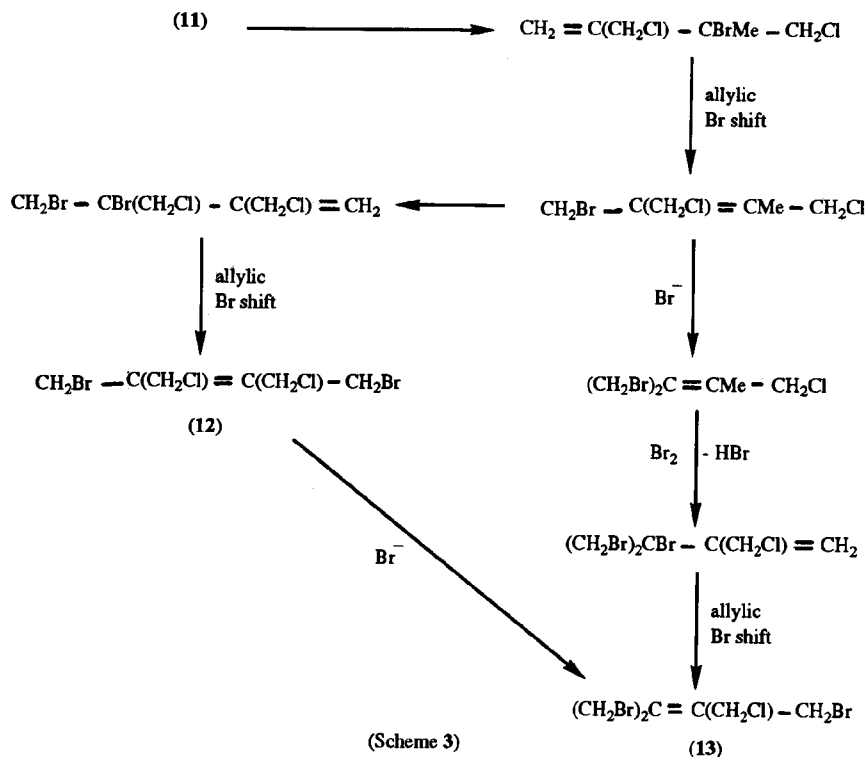
In the present work treatment of (2) with an equimolar quantity of bromine in carbon



pound (9) (10%) and five minor components (G.L.C. and ^1H N.M.R.). However, fractional dis-

tetrachloride under reflux (2h) gave *meso*-(11) (95%). However, the same ratio of reactants when



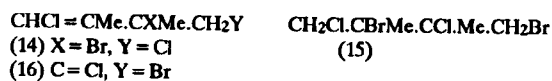


heated under reflux (1h) and then treated with a further equimolar quantity of bromine (1h) afforded 1,4-dibromo-2,3-bis (chloromethyl)but-2-ene (12) (89) and 1,4-dibromo-2-bromomethyl-3-chloromethyl but-2-ene (13) (6%). The latter compound has been made previously (47%) by bromination of diene (3) [1].

The unexpected products (12) and (13) are considered to arise *via* attack on dibromide (11) by bromine acting as a Lewis acid as shown in Scheme 3.

Dehydrobromination of dibromide (11) with powdered potassium hydroxide *in vacuo* at 80°C, with the product being collected as it formed, gave mainly 3-bromo-1,4-dichloro-2,3-dimethylbut-2-ene (14) [δH 6.29 (1H, = CHCl), 3.92 (2H, AB, CH₂Cl) and 2.00 and 1.96 (6H, 2CH₃)].

Dehydrobromination of tetrahalide (15) under comparable conditions had previously given the isomeric trihalogenoalkene (16) [5].

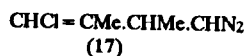


However, when compound (12) was refluxed at low pressure (50 mgh) over an excess of powdered potassium hydroxide, the product was diene (14) (97%) as a mixture of the (*E,E*)- and (*E,Z*)-isomers, respectively in the ratio 5:1; the (*Z,Z*)-isomer was not detected.

(b) 1-chloro-2,3-dimethylbuta-1,3-diene (4)

It has been reported that treatment of either 3,4-dichlorobut-1-ene or 1,4-dichlorobut-2-ene with powdered potassium hydroxide at 90°C afforded 1-chlorobuta-1,3-diene in good yield [6]. In the present work treatment of the 3,4-dichloride (5) with powdered potassium hydroxide at 85°C (ca. 40 mmHg, 1h) gave diene (4) (35%) as a mixture of two isomers in the ratio 1:13 while similar treatment of the 1,4-dichloride (2) afforded unchanged (2) (51% recovered) and diene (4) (100%) as mixture of the same isomers in the ratio 1:70.

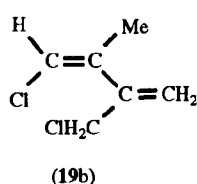
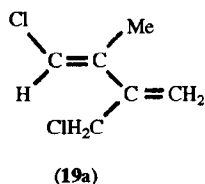
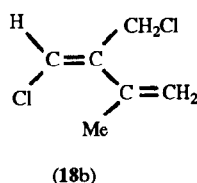
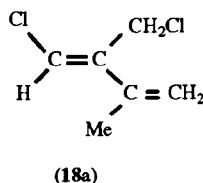
The (*E*) and (*Z*) isomers of compound (4) have been prepared previously in reasonable yield (50) by reaction of the diazo compound (17) with mercury (II) iodide [7].



The I.R. and $^1\text{H-NMR}$ spectra of a major isomer prepared in the present work were identical to those reported [7] for the (*E*)-isomer.

(c) 1-Chloro-2-chloromethyl-3-methylbuta-1,3-diene (18) and 1-chloro-3-chloromethyl-2-methylbuta-1,3-diene (19)

Separate treatment of the trichloride (8) and a mixture of the trichloride (7) and (8) with powdered potassium hydroxide at 100°C under reduced pressure gave recovered trichloride (13% and 20%, respectively) and a mixture (99% and 88%, respectively) of three of the four possible isomers of dienes (18) and (19) in the ratio 1:1:15.



On steric grounds, the major product would be expected to be the (*Z*)-isomer (18a) or the (*E*)-isomer (19a) with the chlorine *trans* to the alkene grouping $\text{CH}_2=\text{C}(\text{CH}_2\text{X})$ ($\text{X}=\text{H}$ or Cl) as found for the synthesised major isomers of dienes (4) and (10); this was confirmed by the low field $=\text{CHCl}$ $^1\text{H-NMR}$ absorption (δ 6.38), cf (4a) δ 6.18 and (10) δ 6.22. The $^1\text{H-NMR}$ spectrum of the Diels-Alder adducts of the diene mixture with tetracyanoethylene (see later) indicated that the major diene had structure (18) and so it is identified as the (*Z*)-isomer (18a). The two minor isomers are probably the corresponding (*E*)-diene (18b) and the (*E*)-diene (19a).

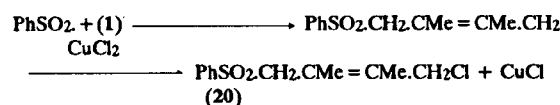
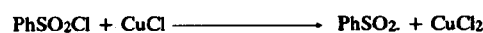
Reactions of the chlorodienes

(a) With benzenesulphonyl chloride

The copper-catalysed additions of alkane- and arene-sulphonyl chlorides to olefins to give 1:1

adducts [8,9] has been extended to the reaction of benzenesulphonyl chloride with 1,3-dienes [8,10] and conjugated trienes [10]. With 1,3-dienes, including buta-1,3-diene and 2-methylbuta-1,3-diene, it was observed that 1,4-adducts were formed and *anti*-addition via initial benzenesulphonyl radical attack was postulated [8,10].

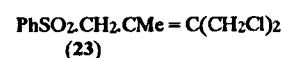
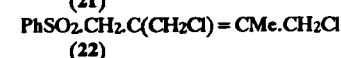
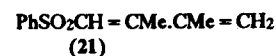
In the present work the reaction between diene (1) and benzenesulphonyl chloride in acetonitrile in the presence of copper (I) chloride and triethyl-ammonium chloride at 90°C was first investigated. This gave 1-(benzenesulphonyl)-4-chloro-2,3-dimethylbut-2-ene (20) (92%) and the following modified version of the original postulated mechanism is proposed.



The $^1\text{H-NMR}$ spectrum of the sulphone (20) showed quartet splitting (J 1.5 Hz) for the two methyl groups indicating that they were *cis* and that the product is probably the (*Z*)-isomer.

Triethylamine in benzene has been used successfully for elimination of hydrogen chloride from such 1,4-adducts to give 1-(benzenesulphonyl)-1,3-dienes [8]. Treatment of adduct (20) with triethylamine (1:1 molar ratio) in toluene at 0°C gave triethyl-ammonium chloride (96%) and a white crystalline compound (92%) which, on storage overnight, changed to an elastomer identified as poly [1-(benzenesulphonyl)-2,3-dimethylbutadiene]; the initial white crystalline product is therefore considered to be diene (21). The polymerisation may have been initiated by atmospheric oxygen or by traces of triethylamine in the monomer.

The reaction of diene (3) with benzenesulphonyl chloride under similar conditions gave a mixture of the two 1,4-adducts (22) (28%) and (23) (17%).



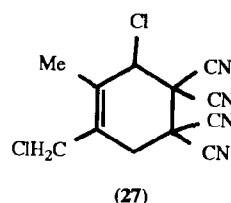
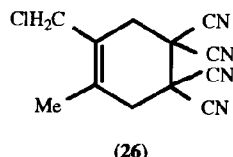
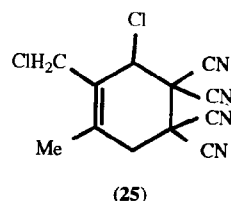
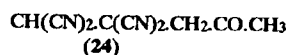
This result is consistent with previous observation that PhSO_2 radical attack is favoured at the more electron-rich double bond of a diene [8].

Attempted reaction of diene (4) with benzenesulphonyl chloride under comparable conditions gave an intractable black tar.

(b) With tetracyanoethylene

Reaction of buta-1,3-diene or diene (1) with tetracyanoethylene (TCNE) is reported to occur readily in acetone as solvent at 0°C to give the corresponding Diels-Alder adducts in good yield [11]. However, reaction involving diene (3) gave the 1:1 adduct (24) of acetone and TCNE [12] (76%) which indicates that substitution of a CH_3 group by a CH_2Cl group markedly deactivates the diene towards Diels-Alder adduct formation. When the reactants were heated in benzene at 80°C the adduct (25) (75%) was obtained. Under similar conditions the diene (18) or (19) gave an adduct (90%), the $^1\text{H-NMR}$ spectrum of which showed multiplet splitting for the CHCl absorption while the CH_2Cl group appeared as an AB pattern (J 9.4 Hz) with further splitting; a singlet methyl absorption and a ring methylene (dd) absorption were also present. The AB pattern for the CH_2Cl absorption indicates that it is close to an asymmetric centre and this is confirmed by the observed coupling between the CH_2Cl protons and the methine proton. This is strong evidence for the adduct having structure (26) formed from diene (18), rather than the alternative structure (27) arising from diene (19).

Attempted reaction of diene (4) with TCNE under the same conditions gave unchanged (4) (45% recovered), unchanged TCNE (49% recovered) and an intractable black solid residue.



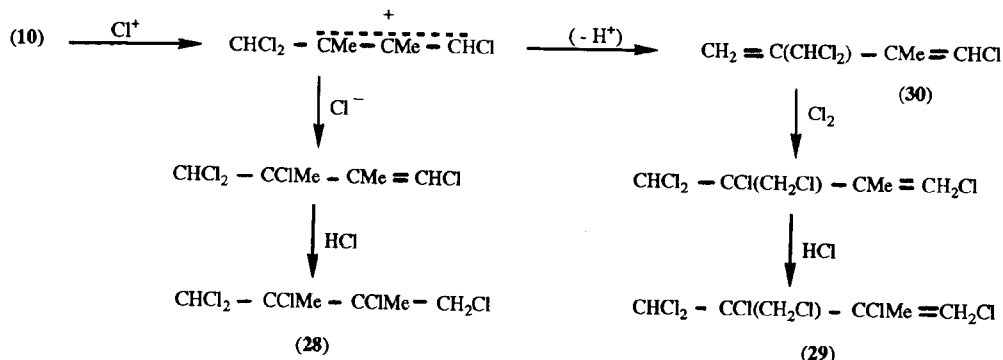
Diene (10) under the same conditions gave unchanged TCNE (100% recovered).

The reluctance of dienes (4) and (10) to give adducts with TCNE is surprising in view of the successful reaction with diene (18).

(c) Miscellaneous reactions

Chlorine gas when bubbled slowly into a solution of diene (10) in carbon tetrachloride gave 1,1,2,3,4-pentachloro-2,3-dimethylbutane (28) (34.5%), a 1:1 mixture of *erythro*- and *threo*-1,1,2,3,4-pentachloro-2-chloromethyl-3-methylbutane (29) (33%), and higher-boiling material.

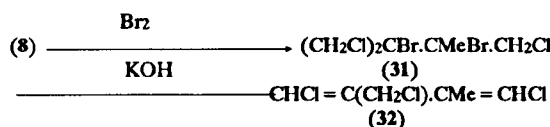
The formation of these products in high yield was unexpected since they arise *via* addition of hydrogen chloride. Minor products only arising from hydrogen chloride addition were observed in the reaction of diene (1) with chlorine gas [1]. Compound (28) and (29) are probably formed as shown in Scheme 4.



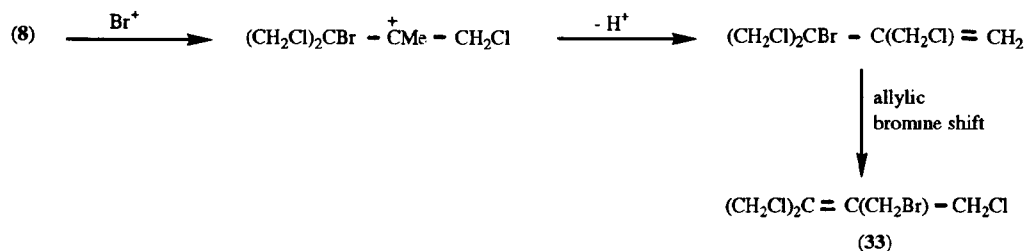
(Scheme 4)

Insufficient hydrogen chloride is produced in the formation of intermediate (30) to account for both products (28) and (29) and so it is proposed that further substitutive chlorination, e.g. of (30) occurs, and that such intermediates undergo further chlorination to give the observed higher-boiling material.

The bromination of trichloride (88) was also investigated since the expected dibromide (31) was a precursor to 1,4-dichloro-2-chloromethyl-3-methylbuta-1,3-diene (32) i.e.



However, treatment of alkene (8) with a slight excess of bromine in dichloromethane under reflux gave the tetrahalide (35) (95%) formed by substitutive bromination, i.e.



This result was unexpected and in marked contrast to the straight forward addition of bromine across that double bond of dichloride (2).

Experimental

The techniques used were as described previously [5], except that for G.L.C. a Pye 104 instrument was employed with columns (2 or 4 m) packed with Apiezon L grease (APL), polythylene glycol adipate (PEGA), or Silicone oil SE30 (10% by weight) on Celite.

Chlorination of 2,3-dimethylbuta-1,3-diene (1)

A solution of chlorine (35.0 g, 0.49 mol) in carbon tetrachloride (300 cm³) was added slowly (2h) to a stirred solution of the diene (50.0 g, 0.61 mol) in carbon tetrachloride (300 cm³) maintained

at -20°C. Removal of the solvent and unreacted diene (21.9 g, 0.26 mol, 43% recovered) gave a higher-boiling residue (59.5 g) which, on a distillation at reduced pressure through a spinning-band column, yielded (i) 2-chloromethyl-3-methylbuta-1,3-diene (3) (6.0 g, 52.0 mmol, 15%), b.p. 30-32°C at 10 mmHg (lit., [1] 25-27°C at 9 mmHg), (ii) a mixture (0.98 g), b.p. 32-60°C at 10 mmHg, of (3) (0.43 g, 3.6 mmol, 1%) and 3,4-dichloro-2,3-dimethylbut-1-ene (5) as shown by i.r. spectroscopy and g.l.c. (2m APL at 150°C), (iii) (5) (2.08 g, 17.7 mmol, 5%) (Found: C, 46.8; H, 6.6; Cl, 46.6. Calc. for C₆H₁₀Cl₂: C, 47.0; H, 6.6; Cl, 46.3%), b.p. 60-62°C at 10 mmHg, which was identified by a comparison of its ¹H-NMR spectrum with that reported [7] (iv) *trans*-1,4-dichloro-2,3-dimethylbut-2-ene (2) (25.5 g, 0.167 mol, 48%), b.p. 74-76°C at 10 mmHg (lit [1] 70-71°C at 10 mmHg), m.p. 32-34°C, (v) a mixture (7.46g, 39.7 mmol, 11%) (Found: C, 38.9; H, 4.9; Cl, 576.2. Calc. for C₆H₉Cl₃: C, 38.4; H, 4.8; Cl, 56.8%), b.p. 86-88°C at 3 mmHg, of two components in the ratio 1:1 (G.L.C. 2M APL at 150°C)

identified by ¹H-NMR spectroscopy as 3,4-dichloro-2-chloromethyl-3-methylbut-1-ene (7) (3.73 g, 19.8 mmol, 5.5%); ¹H-NMR δ 5.73 (1H, s, CH=), 5.53 (1H, s, CH=), 4.28 (2H, s, CH₂Cl), 3.88 (2H, AB, CH_AH_BCl, J_{AB} 13 Hz), and 1.87 (3H, s, CH₃) p.p.m, m/z 190, 188 and 186 (7%, M⁺), and 79 (100%, C₆H₇⁺), and 1,4-dichloro-2-chloromethyl-3-methylbut-2-ene (8) (3.73 g, 19.8 mmol, 5.5%), (vi) 1,4-dichloro-2-chloromethyl-3-methylbut-2-ene (8) (6.95 g, 37.9 mmol, 10.5%) (Found: C, 38.8; H, 5.0; Cl, 57.0. C₆H₉Cl₃ requires C, 38.4; H, 4.8; Cl, 56.8%), b.p. 84-86°C at 2 mmHg; ¹H-NMR δ 4.29 (2H, s, CH₂Cl), 4.27 (2H, s, CH₂Cl), 4.15 (2H, s, CH₂Cl), 4.15 (2H, s, CH₂Cl), and 1.98 (3H, s, CH₃), m/z 190, 188 and 186 (28%, M⁺), and 39 (100%, C₃H₃⁺), and (vii) a black solid residue (9.63 g).

Thermal isomerisation of a mixture of 3,4-dichloro-2-chloromethyl-3-methylbut-1-ene (7) and 1,4-dichloro-2-chloromethyl-3-methylbut-3-methylbut-2-ene (8)

An equimolar mixture of the two dichlorides was sealed in an NMR tube and heated at 105°C. The reaction was monitored by examination of the ¹H-NMR spectrum at regular intervals. A gradual disappearance of the bands assigned to the but-1-ene was observed and after a period of 362h the ratio of the but-2-ene (8) to but-1-ene (7) was 98:2; this ratio was unchanged after heating for a further 113h at 105°C.

Chlorination of 1,4-dichloro-2,3-dimethylbut-2-ene (2)

Dry chlorine gas was slowly passed into a solution of the dichloride (6.33 g, 41.3 mmol) in dichloromethane (50 cm³) at room temperature (90 min). Removal of the solvent at reduced pressure (70 mmHg) at room temperature gave higher-boiling material (8.13 g) which was shown by G.L.C. (2M APL at 150°C) to contain one major (ca. 84%) and several minor components. The major component was identified as 3,4-dichloro-2-chloromethyl-3-methylbut-1-ene (7) (ca. 6.5 g, ca. 34.6 mmol, ca. 84%) by ¹H-NMR spectroscopy. In an attempt to obtain a pure sample of compound (7) the mixture (6.90 g) was distilled at reduced pressure to give the following fractions all of which were examined by g.l.c. (2m SE30 oil at 170°C); (i) a mixture (2.70 g), b.p. 40-76°C at 1 mmHg, of unchanged dichloride (2) (0.24 g, 1.5 mmol, 4% recovered), a trichloride C₆H₉Cl₃, tentatively identified as 3,4-dichloro-3-chloromethyl-2-methylbut-1-ene (6) (0.45 g, 2.4 mmol, 7%) by G.L.C. - mass spectrometry; *m/z* 190, 188, and 186 (9%, M⁺), 154, 152 and 150 [55% (M-HCl)⁺], 141, 139 and 137 [27%, (M-CH₂Cl)⁺], 118 and 116 [35%, (M-Cl)⁺], 117 and 115 [25% (M-HCl₂)⁺] and 79 (100%, C₆H₇⁺), 3,4-dichloro-2-chloromethyl-3-methylbut-1-ene (7) (0.68 g, 3.3 mmol, 10%), and 1,4-dichloro-2-chloromethyl-3-methylbut-2-ene (8) (1.36 g, 7.2 mmol, 20%) in the ratio 1.0:1.5:2.1:4.5, (ii) (8) (2.52 g, 13.4 mmol, 38%), b.p. 74-76°C at 1 mmHg (iii) a mixture (0.44 g), b.p. 76-78°C at 1 mmHg of a solid and a liquid which was filtered to afford a filtrate of (8) (0.14 g, 9.74 mmol, 2%) and crystals of 1,4-dichloro-2,3-bis(chloromethyl) but-2-ene (9) (6.30

g, 1.3 mmol, 4%), m.p. (from petroleum ether (b.p. 40-60°C)) 108-110°C (lit. [1] 106-108°C), and (iv) a residue (1.36 g) b.p. 78°C at 1 mmHg which was washed with acetone and filtered to give (9) (0.50 g, 2.2 mmol, 6%).

Reaction of trans-1,4-dichloro-2,3-dimethylbut-2-ene (2) with bromine

(a) Experiment 1

To a solution of the alkene (2) (2.52 g, 16.4 mmol) in carbon tetrachloride (100 cm³) was slowly added bromine (3.20 g, 20.0 mmol) and the resultant mixture was heated under reflux (2h). The solvent was removed under reduced pressure (ca. 70 mmHg) and the resultant mixture (5.54 g) of liquid and solid was filtered and the solid recrystallized from petroleum ether (b.p. 60-80°C) to afford 2,3-dibromo-1,4-dichloro-2,3-dimethylbutane (11) (4.84 g, 15.4 mmol, 95%), m.p. 110-113°C (lit., [1] 109-110°C).

(b) Experiment 2

To a solution of the alkene (2) (2.23 g, 14.5 mmol) in carbon tetrachloride (100 cm³) heated under reflux was slowly added (1h) (a solution of bromine (2.34 g, 14.6 mmol) in carbon tetrachloride (200 cm³)). A further amount of neat bromine (1.76 g, 11.0 mmol) was then added and heating was continued (1h). Removal of the solvent and unreacted bromine at reduced pressure (ca. 70 mmHg) gave a mixture (5.04 g) of solid and liquid. The solid was filtered and recrystallized from petroleum ether (b.p. 60-80°C) to afford (i) colourless crystals of 1,4-dibromo-2,3-bis(chloromethyl) but-2-ene (12) (4.02 g, 12.9 mmol, 89%) (Found: C 23.4; H, 2.6; Cl, 22.8; Br, 49.1. Calc. for C₆H₈Br₂Cl₂: C, 23.1; H, 2.5; Cl, 22.8; Br, 51.4%), m.p. 123-5°C, the ¹H-NMR and mass spectra of which were comparable to those reported previously [1] and (ii) a filtrate (0.9 g) which, on storage, slowly deposited colourless crystals of 1,4-dibromo-2-bromomethyl-3-chloromethylbut-2-ene (13) (0.032 g, 0.90 mmol, 6%) (Found: C, 20.5; H, 2.3; halogen 77.5% Calc. for C₆H₈Br₃Cl: C, 20.2; Cl, 10.0; Br, 67.5%), m.p. (from petrol) 132-134°C [lit., [1] m.p. (capillary) 136-138°C], ¹H-NMR δ 4.20 (2H, s, CH₂Cl) and 4.14 (6H, s, 3CH₂Br) p.p.m.; the I.R. and mass spectra were in agreement with those reported [1].

Preparation of 1,4-dichloro-2,3-dimethylbuta-1,3-diene (10)

2,3-dibromo-1,4-dichloro-2,3-dimethylbutane (11) (5.59 g, 7.8 mmol) was intimately mixed with an excess of powdered potassium hydroxide (16 g) and the reaction mixture was heated to 80°C under reflux at reduced pressure (ca. 50 mmHg) under nitrogen (3H). The reaction flask was maintained at 80°C for a further period (3h) while the products were collected at 196°C *in vacuo*. The resultant material was dried (molecular sieve type 4A, 24h) and was identified as 1,4-dichloro-2,3-dimethylbuta-1,3-diene (10) (2.60 g, 17.21 mmol, 97%) (Found: C, 47.5; H, 5.3; Cl, 46.0. Calc. for C₆H₈Cl₂; C, 47.6; H, 5.2; Cl, 47.0%); the ¹H-NMR spectrum and g.l.c. (2m APL at 150°C) showed the presence of two isomers in the ratio 1:5. The major isomer was separated by G.L.C. (3m SE 30 oil at 120°C) and was identified as (*E,E*)-1,4-dichloro-2,3-dimethylbuta-1,3-diene (10) (2.10 g, 13.9 mmol, 81%) (Found: C, 47.5; H, 5.5; Cl, 46.9%), ¹H-NMR δ 6.22 (1H, complex, CHCl) and 1.98 (3H, complex Me), ppm m/z 154, 152 and 150 (100%, M⁺) and 117 and 115 [72%, (M-Cl)⁺], U.V. (hexane) λ_{max} 240 (ε 30, 300) and λ_{inf} 237 (ε 30, 200) nm. The minor isomer could not be obtained pure but was identified as (*E,Z*)-1,4-dichloro-2,3-dimethylbuta-1,3-diene (10) (0.50 g, 3.31 mmol, 16%) by its ¹H-NMR spectrum: δ 6.06 (1H, complex, CHCl), 5.81 (1H, complex, CHCl) and 1.95 (6H, complex, 2Me) p.p.m.

Preparation of 1-chloro-2,3-dimethylbuta-1,3-diene (4)

A mixture of 3,4-dichloro-2,3-dimethylbut-1-ene (5) (3.90 g, 25.4 mmol) and powdered potassium hydroxide (10 g) was heated under reflux (ca. 85°C at reduced pressure (ca. 40 mmHg, 1h). A further amount of powdered potassium hydroxide (10 g) was then added and heating was continued (2h). The volatile product was dried (molecular sieve type 4A) and was identified as 1-chloro-2,3-dimethylbuta-1,3-diene (4) (2.82 g, 24.2 mmol, 95%) (Found: C 62.0; H, 8.0; Cl, 30.1. C₆H₉Cl requires C, 61.8; H, 7.8; Cl, 30.40%); λ_{max} (hexane) 227 (ε 12,420) and 234 (ε 13,300) nm, m/z 118 and 116 (77%, M⁺) and 81 [100%, (M-Cl)⁺]; G.L.C. (2m APL at 120°C) showed the presence of two isomers in the ratio 1:13 assigned to the (*Z*)- and (*E*)-isomers, respectively, and the ¹H-NMR spectrum was in agreement with those reported for two isomers [7].

A second reaction using a mixture of 1,4-dichloro-2,3-dimethylbut-2-ene (2) (10.3 g, 67.3 mmol) and powdered potassium hydroxide (30 g) which was heated (3h) under reflux at reduced pressure (ca. 18 mmHg) gave unchanged starting alkene (2) (5.28 g, 34.6 mmol, 41% recovered) and a mixture of (*Z*)- and (*E*)-1-chloro-2,3-dimethylbuta-1,3-diene (4) (3.80 g, 32.6 mmol, 99%) in the ratio 1:70 (G.L.C., as before).

Reaction of 1,4-dichloro-2-chloromethyl-3-methylbut-2-ene (8) with bromine

A mixture of the olefin (8) (2.98 g, 15.8 mmol), bromine (2.69 g, 16.8 mmol), dichloromethane (150 cm³), and lithium bromide (0.1) was heated under reflux (5h). Removal of the solvent and excess of bromine under reduced pressure (ca. 70 mmHg) gave a solid which was recrystallized from petroleum ether (b.p. 40-60°C) and identified as 1,4-dichloro-2-bromomethyl-3-chloromethylbut-2-ene (33) (5.30 g, 15.3 mmol, 95%) (Found: C, 27.1; H, 2.9; Cl, 39.8; Br, 30.1. C₆H₈BrCl₃ requires C, 27.0; H, 3.0; Cl, 39.0; Br, 30.0%), m.p. 117-118°C, ¹H-NMR (10% solution in CCl₄) 4.21 (6H, s, 3CH₂Cl) and 4.00 (2H, s, CH₂Br) p.p.m., m/z 270, 268, 266 and 264 (19% M⁺), 191, 189, 187 and 185 [48%, (M-Br)⁺], and 153, 151 and 149 100% [(M-HBrCl)⁺].

Reaction of 1,4-dichloro-2-chloromethyl-3-methylbut-2-ene (8) with potassium hydroxide

A mixture of the alkene (8) (1.65 g, 8.8 mmol) and an excess of powdered potassium hydroxide (5.0 g), slowly heated to 100°C (90 min) under nitrogen at reduced pressure (15 mmHg) and maintained at this temperature (90 min), gave unchanged alkene (0.22 g, 1.1 mmol, 13% recovered) and a lower boiling fraction (1.15 g, 7.6 mmol, 99%) (Found: C, 47.3; H, 5.3; Cl, 47.2. Calc. for C₆H₈Cl₂; C, 47.4; H, 5.2; Cl, 47.0%) which was dried (molecular sieve type 4A) and shown by g.l.c. (2m APL at 120°C) mass spectrometry to consist of three of the four possible isomers of 1-chloro-2-chloromethyl-3-methylbuta-1,3-diene and 1-chloro-3-chloromethyl-2-methylbuta-1,3-diene in the ratio 1:1:15. The major isomer was separated by G.L.C. and was tentatively identified as (*Z*)-1-chloro-2-chloromethyl-3-methylbuta-1,3-diene (18a) (1.02 g, 6.8 mmol, 87%) (Found: C 47.4; H, 5.4; Cl, 47.2%) λ_{max} 5.18 and 6.25s (conj. C=C str.) μm, λ_{max} (hexane) 235 (ε 14,100) nm, ¹H-NMR δ 6.38 (1H,

m, CHCl₃), 5.32 (2H, m, : CH₂), 4.20 (2H, s, CH₂Cl), and 1.98 (3H, s, CH₃) p.p.m, m/z 154, 152 and 150 (100%, M⁺), 117 and 115 and 79 (99%, C₆H₇⁺).

A second experiment in which a mixture of 3,4-dichloro-2-chloromethyl-3-methylbut-1-ene (7) (0.33 g, 1.76 mmol) and 1,4-dichloro-2-chloromethyl-3-methylbut-2-ene (8) (2.97 g, 15.8 mmol) was treated with an excess of powdered potassium hydroxide (10 g) at 100°C (as before) gave unchanged alkene (0.67 g 3.57 mmol, 20% recovered) and a mixture (2.10 g, 13.9 mmol, 99%) of the same diene isomers in the ratio 1:1:15.

Reaction of 2,3-dimethylbuta-1,3-diene (1) with benzenesulphonyl chloride

A mixture of the diene (1) (13.8 g, 0.168 mol), freshly distilled benzenesulphonyl chloride (29.8 g, 0.168 mol), and acetonitrile (6.8 g, 0.158 mol) was efficiently stirred and heated at 90°C (90 min). The reaction mixture was cooled (ca 5°C). Pre-cooled (ca., 5°C) methanol (80 cm³) was added and the resultant mixture was filtered. Removal of the bulk of the methanol from the filtrate at reduced pressure (100 mmHg) followed by filtration afforded a solid which was recrystallized from ethanol to give colourless crystals of 1-(benzenesulphonyl)-4-chloro-2,3-dimethylbut-2-ene (20) (40.0 g, 0.154 mol, 92%) (Found: C, 55.4; H, 5.8; S, 12.2; Cl, 13.7. C₁₂H₁₅DO₂Cl requires C, 55.7; H, 5.8; S, 12.4; Cl, 13.7%), m.p. 82-4°C ¹H-NMR δ 7.60 (5H, mult, C₆H₅), 3.95 (2H, s, CH₂SO₂), 3.74 (2H, s, CH₂Cl), 1.91 (3H, s, MeC.CH₂, J 1.3 Hz), and 1.35 (3H, s, Me C.CH₂Cl, J 1.3 Hz) p.p.m., m/z 223 [4% (M-Cl)⁺], 119 and 117 [100, (M-PhSO₂)⁺].

Reaction of 1-(Benzenesulphonyl)-4-chloro-2,3-dimethylbut-2-ene (20) with triethylamine

A solution of the alkene (20) (5.28 g, 20.4 mmol) in toluene (50 cm³) was treated with triethylamine (2.10 g, 20.7 mmol) at 0°C and the mixture was stirred at room temperature (70h). The resulting material was filtered to give triethylammonium chloride (2.74 g, 19.9 mmol, 96%) and the toluene and excess of amine were removed from the filtrate *in vacuo* at room temperature. This afforded a white crystalline residue which changed overnight in air into a rubbery material identified as poly [1-(benzenesulphonyl) (-2,3-dimethylbuta-1,3-diene)]

(4.20 g, 92%) [Found: C, 64.8; H, 6.4; S, 14.2 (C₁₂H₁₄SO₂)_n requires C 64.8; H, 6.3; S, 14.4%], m.p. 150°C.

Reactions of 2-chloromethyl-3-methylbuta-1,3-diene (3) with benzenesulphonyl chloride

A mixture of the diene (3) (2.24 g, 19.2 mmol), benzenesulphonyl chloride (3.42 g, 19.2 mmol), cuprous chloride (0.024 g, 0.25 mmol), triethylammonium chloride (0.033 g, 0.24 mmol), and acetonitrile (0.87 g, 21.0 mmol) was heated at 90°C (2.5 h) during which time the colour of the solution changed from bright yellow to orange and then to brown. Treatment of the resultant solution with ethanol (10 cm³) failed to precipitate any solid. The ethanolic solution was then washed with water (50 cm³) and extracted with chloroform (50 cm³). Removal of the chloroform under reduced pressure (ca. 20 mmHg) afforded a dense liquid (5.20 g) which partially solidified on storage at room temperature (12 h). The solid was filtered, was recrystallized from benzene-petroleum ether (b.p. 60-80°C), and was identified as a mixture (2.53, 8.63 mmol, 54%) (Found: C, 49.2; H, 4.9; S, 11.1; Cl, 24.5 Calc. for C₁₂H₁₄SO₂Cl₂; C, 49.2; H, 4.7; S, 10.9; Cl, 24.2%), m.p. 75-77°C, m/z 259 and 257 [7%, (M-Cl)⁺], 155, 153 and 151 [75%, (M-PhSO₂)⁺], 154, 152 and 150 [89%, (M-PhSO₂H)⁺] and 77 (100%, C₆H₅⁺), of 1-(benzenesulphonyl)-4-chloro-3-chloromethyl-2-methylbut-2-ene (23) (1.60 g, 5.45 mmol, 28%) and 1-(benzenesulphonyl)-4-chloro-2-chloromethyl-3-methylbut-2-ene (22) (0.93 g, 3.18 mmol, 17%) by ¹H-NMR spectroscopy with bands for PhSO₂.CH₂CMe:C(CH₂Cl)₂ at δ 7.49 to 7.93 (5H, mult, pH), 4.18 (2H, s, CH₂SO₂), 3.88 (2H, s, CH₂Cl) 3.78 (2H, s, CH₂Cl), and 1.96 (3H, s, CH₃) p.p.m. and bands for PhSO₂.CH₂C(CH₂Cl):CMe.CH₂Cl at δ 7.93 to 7.49 (5H, m, Ph), 4.29 (2H, s, CH₂SO₂), 4.04 [2H, s, CH₂Cl (a)], 3.90 [2H, s, CH₂Cl (b)] and 1.45 (3H, s, CH₃) p.p.m.

c) With tetracyanoethylene

A mixture of the diene (3) (0.55 g, 4.7 mmol), tetracyanoethylene (0.61 g, 4.7 mmol), and benzene (30 cm³) was heated under reflux (2.5 h). Removal of benzene (15 cm³) gave a solid identified as unchanged tetracyanoethylene (0.05 g, 0.3 mmol, 6.5%). When the remaining benzene was removed under reduced pressure (ca. 5 mmHg) a solid was obtained which was recrystallized from benzene

and was identified as 1-chloromethyl-2-methyl-4,4,5,5-tetracyanocyclohexane (**25**) (0.86 g, 3.5 mmol, 75%) (Found: C, 59.0; H, 3.8; N, 23.4. $C_{12}H_9ClN_4$ requires C, 58.9; H, 3.7; N, 23.9%), m.p. 129-31°C, m/z 246 and 244 (52%, M^+) and 209 [100%, (M-Cl) $^+$]. 1H -NMR (25% solution in acetone- d_6) δ 4.38 (2H, s, CH_2Cl), 3.50 (4H, s, $2CH_2$), and 2.00 (3H, s, CH_3) p.p.m.

Reaction of 1,4-dichloro-2,3-dimethylbuta-1,3-diene (10) with chlorine

A mixture (1.56 g, 10.3 mmol) of the (*E,E*) and (*E,Z*)-diene isomers (ratio 5:1) in carbon tetrachloride (30 cm^3) was stirred at room temperature while chlorine gas was bubbled into the solution at a moderate rate (75 min). Removal of the solvent under reduced pressure (50 mmHg) gave a liquid (2.3 g) which was shown by G.L.C. (2m APL at 200°C) to consist of three compounds in the ratio 2:1:1. Distillation of the liquid gave (i) 1,1,2,2,4-pentachloro-2,3-dimethylbutane (**28**) (0.92 g, 3.55 mmol, 34.5%) (Found: C 27.3; H, 3.3; Cl, 69.5. $C_6H_9Cl_5$ requires C, 26.8; H, 3.3; Cl, 69.9%), b.p. 78-80°C at 0.5 mmHg, 1H -NMR bands at δ 6.18 (1H, s, $CHCl_2$), 4.05 (2H, s, CH_2Cl), and 1.99 (6H, s, $2CH_3$) p.p.m. m/z 211, 209 and 207 [9%, (M- CH_2Cl) $^+$] and (ii) 1,1,3,4-pentachloro-2-chloromethyl-3-methylbutane (**29**) (0.99 g, mmol, 33%) (Found: C 38.4; H, 4.5; Cl, 57.2. $C_6H_8Cl_6$ requires C 38.6; H, 4.3; Cl, 57.1%), b.p. 100-15°C at 0.5 mmHg, 1H -NMR δ 6.41 (1H, $CHCl_2$), 4.25 (4H, $2CH_2Cl$), and 2.11 (3H, CH_3) p.p.m. as a mixture of the *erythro* - and *threo*-isomers in the ratio 1:1 (g.l.c., 2m APL at 200°C); the mass spectra of the two isomers were almost identical with bands at m/z 213, 211, 209, and 207 [ca. 45% (M- $CHCl_2$) $^+$] and 177, 175, 173 and 171 (100%, $C_5H_5Cl_3^+$), and (iii) a black residue (0.40 g), b.p. 105°C at 0.5 mmHg, which was not investigated further.

Reaction of 1-chloro-2-chloromethyl-3-methylbuta-1,3-diene (18) with tetracyanoethylene

A mixture of the diene (**18**) (1.10g, 7.28 mmol) and tetracyanoethylene (0.93 g, 7.26 mmol)

in benzene (35 cm^3) was heated under reflux (3h). Removal of the majority of the solvent (30 cm^3) under reduced pressure gave unchanged tetracyanoethylene (0.18 g, 1.4 mmol, 18.5% recovered) and a filtrate from which the remaining solvent was removed under reduced pressure. The resulting semi-solid material (1.82 g) was recrystallized from a 1:1 mixture of benzene and petroleum ether (b.p. 40-60°C) to give colourless crystals of 6-chloro-1-chloromethyl-2-methyl-4,4,5,5-tetracyanocyclohexene (**26**) (1.45 g, 5.2 mmol, 90%) (Found: C, 51.6; H, 2.8; N, 20.0; Cl, 25.4. $C_{12}H_8Cl_2N_4$ requires C, 51.6; H, 2.9; N, 20.0; Cl, 25.5%), m.p. 136-8°C, m/z 282, 280 and 278 (10%, M^+) and 154, 152 and 150 (100%, $C_6H_8Cl_2^+$), 1H -NMR (25% solution in acetone- d_6) δ 5.88 (1H, mult, $CHCl$), 4.87 (2H, AB mult, CH_2Cl , J_{AB} 9.4 Hz), 3.64 (2H, dd, CH_2), and 2.09 (3H, s, CH_3) p.p.m.

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