Studies of Geometrical Isomerism in Some Chloro- and Dichloro-olefins by Nuclear Magnetic Resonance Methods

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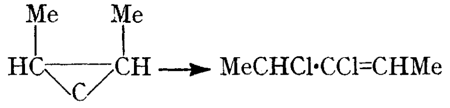
N.m.r. parameters for chloro- and dichloro-propenes, -butenes, and -pentenes have been measured. Unambiguous geometrical assignments have been made on the basis of established n.m.r. methods combined with an extended version of the model-compound approach. Solvent shifts are also recorded.

STUDIES[1] of the solvolysis of *gem*-dichlorocyclopropanes in ethanolic silver nitrate have shown that the cyclopropane ring opens to *trans*-chloro-olefins and this specificity has been explained by reference to the selection rules of Woodward and Hoffman[2] for electrolytic reactions. The analogous liquid- and gas-phase pyrolysis of some alkyl-substituted *gem*-dihalogenocyclopropanes[3,4] has shown that isomerisation to dichloro-olefins is the main reaction, although subsequent decomposition to chlorodienes can occur. However the assignment of the configurations of the products from these reactions was either lacking or has been found to be incorrect.[3a] A kinetic study[5] of the thermal isomerisation of *cis*- and *trans*-1,1-dichloro-2,3-dimethylcyclopropane to a single isomer (1a) of 3,4-dichloropent-2-ene presented the problem of an unambiguous assignment of the stereochemistry of this olefin and of those produced in similar reactions. We have investigated the n.m.r. spectra of (1a) and its geometric isomer (1b) and a number of closely related propenes, butenes, and pentenes and have examined the available methods[6-12] of correlating the n.m.r. parameters with the stereochemistry of these olefins. To ensure a certain assignment of (1a) an extended version of the model compound approach of Tobey[9] has been developed.



(1a)

EXPERIMENTAL

All n.m.r. spectra were obtained on a 4H-100 JEOL spectrometer operating at 100 MHz with a probe temperature of 26°. Compounds were examined as 10—20% solutions in $CDCl_3$ or C_6H_6 with tetramethylsilane as internal reference. Spectra were analysed on a first-order basis or as AB or ABX systems where appropriate. Double-resonance techniques were employed where suitable to simplify analysis. Chemical shifts are given in p.p.m. and are accurate to $\pm 0{\cdot}005$ p.p.m. and coupling constants are accurate to $\pm 0{\cdot}1$ Hz unless otherwise indicated.

All compounds examined were purified by preparative g.l.c. on a 12 ft. × 0·25 in. 11% di-isodecyl phthalate column which was operated under suitable conditions. Unless otherwise stated commercial samples were obtained.

cis- *and* trans-2-*Chlorobut*-2-*ene and* 2-*Chlorobut*-1-*ene*.—These were prepared by the reaction of an excess of PCl_5 with ethyl methyl ketone[13] at 0°.

cis- *and* trans-1,2-*Dichlorobut*-2-*ene and* 2,3-*Dichlorobut*-1-*ene*.—*trans*-1-Chlorobut-2-ene (K and K Labs., Inc.) was allowed to react with chlorine at 0° to give 1,2,3-trichlorobutane, which was then dehydrochlorinated with 50% aqueous alcoholic KOH. G.l.c. showed that there was

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[5] K. A. W. Parry, unpublished results.

[6] C. Pascual, J. Meier, and W. Simon, *Helv. Chim. Acta*, 1966, **49**, 164.

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[8] U. E. Matter, C. Pascual, E. Pretsch, A. Pross, W. Simon, and S. Sternhell, *Tetrahedron*, 1969, **25**, 2023.

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[10] See ref. 9 for list of references.

[11] J. Niwa, *Bull. Chem. Soc. Japan*, 1967, **40**, 1512.

[12] J. Ronayne and D. H. Williams, *J. Chem. Soc.* (*C*), 1967, 2642.

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50% conversion into 2,3-dichlorobut-1-ene, 15% conversion into *trans*-1,2-dichlorobut-2-ene, and 35% conversion into *cis*-1,2-dichlorobut-2-ene.

cis- *and* trans-3-*Chloropent*-2-*ene*.—These were obtained directly by the reaction of excess of PCl_5 with diethyl ketone at 0°.

cis-1-*Chlorobut*-2-*ene*.—This was obtained by the allylic chlorination of *cis*-but-2-ene [14] (Cambrian Chemicals Ltd.) with chlorine at 0°. The i.r. spectrum was identical to that previously published.[15]

trans-4-*Chloropent*-2-*ene*.—This was prepared in 80% yield from penta-1,3-diene [16] (Koch-Light Laboratories Ltd.) by shaking with concentrated HCl for 12 hr. at room temperature.

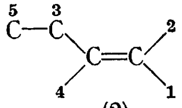
cis-4-*Chloropent*-2-*ene*.—This was obtained from the reaction of *cis*-pent-3-en-2-ol with PCl_3.[15] The *cis*-pent-3-en-2-ol was formed by hydrogenation of pent-3-yne-2-ol [17] by use of a Lindlar catalyst under 60 atm. of hydrogen. The acetylenic alcohol had the following n.m.r. spectrum ($CDCl_3$): 1·41 p.p.m. (3H's) methyl doublet coupled to adjacent CH, *J* 7·0 Hz, 1·82 p.p.m. (3H's) methyl doublet coupled across triple bond to CH, *J* 1·7 Hz, 3·25 p.p.m. (1H) OH proton, and 4·50 p.p.m. (1H) quartet of quartets for CH.

The *cis*-4-chloropent-2-ene formed by chlorination of *cis*-pent-3-en-2-ol with PCl_3 always contained 40% of the *trans*-isomer, even when the products were removed under vacuum through a liquid-air trap. Further purification by g.l.c. was not possible because of *cis–trans*-isomerisation during analysis. This compound has previously been reported [18] as a product of the chlorination of *cis*-pent-2-ene with Bu^tOCl. However, in our hands this reaction gave *trans*-4-chloropent-2-ene and 3-chloro-2-methylbut-1-ene.

cis- *and* trans-3,4-*Dichloropent*-2-*ene*.—This pair of isomers was obtained in two steps: 4-chloropent-2-ene was chlorinated at 0° to give 2,3,4-trichloropentane, which was then dehydrochlorinated with 50% aqueous alcoholic KOH. The product consisted of a *cis–trans*-mixture in the proportion 3 : 1. The *cis*-isomer was purified by distillation to *ca.* 90% purity as preparative g.l.c. caused complete isomerisation to the *trans*-isomer.

DISCUSSION

In the following discussion of n.m.r. data. to permit a clear comparison of various propenes, butenes, and pentenes the numbering shown in (2) will be used. For



(2)

positions 1 and 2 the shifts refer to either a proton or a methyl group.

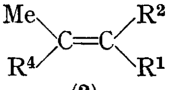
The problem of determining the stereochemistry of di- and tri-substituted ethylenes by n.m.r. methods has been extensively studied.[6-11] Three recent papers [6,7,8] have extended earlier work [10] to a very large number of compounds and two groups of workers, Matter *et al.*[6,7] and Tobey,[9] have derived typical shielding values for various substituents. These substituent constants, $\sigma_{cis\text{-}X}$, $\sigma_{trans\text{-}X}$, $\sigma_{gem\text{-}X}$, are defined as the average shift (in p.p.m.) of a vinyl proton resulting from the introduction of a substituent X in the *cis*-, *trans*-, or *gem*-positions respectively and Table 1 lists these parameters for the CH_3, Cl, and CH_2Cl groups, of relevance to this work. Direct application of these σ constants to the prediction of chemical shifts relies upon a strict additivity of substituent effects, a principle which is not supported by theory [7] and does not hold in practice.[7-9] Deviations from additivity are due to changes in substituent conjugation [8] and conformation and Tobey [9] has evolved a method which allows for such substituent interactions. A model compound is chosen which has known geometry, which differs from the compound of interest only by the lack of a small highly symmetric group such as Me or Cl and has an unambiguous n.m.r. spectrum. Application of the appropriate σ value provides a calculated vinyl chemical shift for the unknown system.

TABLE 1

σ Values [a] taken from the literature

	σ_{cis} [b]	σ_{trans} [b]	σ_{gem} [b]	σ_{cis} [c]	σ_{trans} [c]	σ_{gem} [c]
Cl	0·18	0·13	1·08	0·14 ±0·08	0·09 ±0·11	1·05 ±0·13
Me	−0·22	−0·28	0·45	−0·32 ±0·09	−0·34 ±0·10	0·44 ±0·09
CH_2Cl	0·11	−0·04	0·70			

[a] In p.p.m. Positive value indicates a shift to high frequency. [b] From ref. 7. [c] From ref. 9 with signs reversed.



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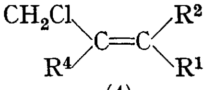

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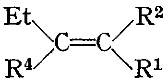

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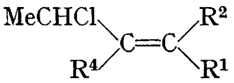

(6)

Key:	R¹	R²	R⁴
a	H	H	H
b	Me	H	H
c	H	Me	H
d	Me	H	Cl
e	H	Me	Cl
f	H	H	Cl

These methods have been applied to the 3,4-dichloropent-2-enes (1a, 1b) assuming initially that (1a) is the *trans*-isomer, (*i.e.*, alkyl groups *trans*) and the calculated σ values are in Table 2. The three model compounds required for calculations (2) and (3) were 2,3-dichlorobut-1-ene (6f) and *trans*- and *cis*-4-chloropent-2-ene (6b, 6c). No n.m.r. data have been reported for (6b) and (6c) and the only assignments for (6f) [4] are probably wrong (see below). Our n.m.r. data for these three compounds are included in Table 3.

Although calculations (1), (2), and (3) (Table 2) all confirm the assignment of (1a) as *trans*-3,4-dichloropent-2-ene the errors in the calculated σ values are of the same order as the chemical shift differences involved and the assignment of (1a) cannot be regarded as very reliable on this basis. There are a number of wrong

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[17] L. I. Smith and J. S. Swenson, *J. Amer. Chem. Soc.*, 1957, **79**, 2962.

[18] C. Walling and W. Thaler, *J. Amer. Chem. Soc.*, 1961, **83**, 3877.

assignments in the literature for simple halogeno-olefins (see below) and in aromatic systems the anomalous nature of halogen substituent effect is very evident.[19] In view of these facts we have extended Tobey's [9] model compound approach to try to obtain more convincing evidence for the assignment of (1a). measured the chemical shifts of [$^2H_1$]2,3-dichloropropene of known geometry and settled the problem of the assignment of δ_1 and δ_2 in this system (4f) which had been in doubt.[25,27] Taking the δ value of ethylene as 5·25, with the σ values of Matter *et al.*[7] (Table 1), we calculated shifts for (4f) to be δ_1 = 5·39 and δ_2 = 5·49.

TABLE 2

Observed and calculated values of δ_1, δ_2, and δ_3 in the 3,4-dichloropent-2-enes (1a, 1b)

Compd.	Position	δ(obs.) [a]	δ (calc.) (1) [b]	(2) [c]	(3) [d]	(4) [e]	Standard deviation calc. (4)
(1a)	δ_2	5·95	5·94 ± 0·2	5·97 ± 0·1	5·82 ± 0·1	5·93	0·06
(1a)	δ_3	4·70				4·66	0·15
(1b)	δ_1	5·77	5·84 ± 0·2	5·77 ± 0·1	*d*	5·85	0·03
(1b)	δ_3	5·14				4·81	0·25

[a] The full list of spectral parameters are given in Table 3 as (6d,6e). [b] From the values of Matter *et al.* (Table 1). [c] By Tobey's method [9] from 2,3-dichlorobut-1-ene (6f) and $\sigma_{gem\text{-}Me}$. [d] By Tobey's method [9] from *trans*-4-chloropent-2-ene (6b) and $\sigma_{trans\text{-}Cl}$. The vinyl chemical shifts in the corresponding *cis*-isomer (6c) were not available since this compound could not be separated from the *trans*-compound. [e] From extended model compound calculations; see text and Table 5.

TABLE 3

Chemical shifts [a] and coupling constants [b] for chloro-olefins

Compound		δ_1	δ_2	δ_3	δ_4	δ_5	J_{12}	J_{13}	J_{14}	J_{23}	J_{24}	J_{34}	J_{35}
Propene	(3a) [c]	4·88	4·96	1·71	5·73		2·1	−1·3	10·0	−1·8	16·8	6·4	
trans-But-2-ene	(3b) [d]	1·63	5·43	1·63	5·43		6·6	1·6	−1·7	−1·7	14·0	6·6	
cis-But-2-ene	(3c) [d]	5·45	1·60	1·60	5·45		6·4	−1·4	7·9	1·2	−1·4	6·4	
trans-2-Chlorobut-2-ene	(3d) [e]	1·70	5·49	2·08			6·6	1·6		−1·2			
cis-2-Chlorobut-2-ene	(3e) [e]	5·62	1·63	2·03			7·1	−1·2		1·2			
2-Chloropropene	(3f) [e,f]	5·11	5·11	2·11			*g*	−0·7		−1·3			
Allyl chloride	(4a)	5·14	5·33	4·05	5·98		1·2	−0·9	10·1	−1·4	16·9	6·6	
trans-1-Chlorobut-2-ene	(4b) [h]	1·73	5·80	4·02	5·61		*g*	*g*	*g*	*g*	*g*	*g*	
cis-1-Chlorobut-2-ene	(4c) [h]	5·71	1·72	4·11	5·63		*g*	*g*	*g*	*g*	*g*	*g*	
trans-1,2-Dichlorobut-2-ene	(4d)	1·80	5·98	4·19			6·6	0·8		0·6			
cis-1,2-Dichlorobut-2-ene	(4e) [i]	5·89	1·78	4·25			7·2	0·3 [j]		0·3 [j]			
2,3-Dichloropropene	(4f) [k]	5·41	5·59	4·16			1·9	0·2 [j]		1·0			
But-1-ene	(5a)	4·85	4·90	2·06	5·86	1·00	1·9	−1·3	10·3	−1·7	17·1	6·2	7·5
trans-Pent-2-ene	(5b) [h]	1·65	5·40	1·94	5·35	0·92	*g*	1·3	1·3	*g*	*g*	*g*	7·5
cis-Pent-2-ene	(5c) [h]	5·37	1·59	2·04	5·34	0·95	*g*	*g*	*g*	0·9	0·9	6·7	6·9
trans-3-Chloropent-2-ene	(5d)	1·71	5·50	2·35		1·11	6·7	1·4		0·6			7·3
cis-3-Chloropent-2-ene	(5e)	5·59	1·64	2·33		1·10	7·2	0·2 [j]		0·6			7·5
2-Chlorobut-1-ene	(5f)	5·12	5·12	2·36		1·14	*g*	0·8		1·6			7·3
3-Chlorobut-1-ene	(6a)	5·09	5·24	4·51	5·96	1·59	1·3	0·6	10·1	0·8	17·1	7·2	6·6
trans-4-Chloropent-2-ene	(6b) [h]	1·70	5·73	4·52	5·63	1·57	6·7	*g*	*g*	*g*	14·9	6·7	6·4
cis-4-Chloropent-2-ene	(6c) [h]	*g*	*g*	4·87	*g*	*g*	*g*	*g*	*g*	*g*	*g*	*g*	6·6
trans-3,4-Dichloropent-2-ene	(6d) [l]	1·79	5·95	4·70		1·68	6·8	0·3 [j]		0·3 [j]			6·8
cis-3,4-Dichloropent-2-ene	(6e) [l]	5·77	1·77	5·14		1·65	7·3	0·2 [j]		0·0			6·6
2,3-Dichlorobut-1-ene	(6f) [m]	5·33	5·53	4·65		1·66	1·8	0·2 [j]		0·5			6·8

[a] In p.p.m. relative to tetramethylsilane. [b] In Hz; signs are assumed, not measured. [c] From ref. 20, in CCl_4. [d] A full analysis of the but-2-enes has been reported [21] for neat liquids. The chemical shifts have been measured in $CDCl_3$, but coupling constants are taken from ref. 21. [e] Solvent shifts are reported in ref. 12 but no absolute chemical shifts. [f] Spectrum has been measured at 40 MHz [22,23] and, for the neat liquid, at 60 MHz.[24] [g] Not measured. [h] Full analysis of A_nXYK_m systems was not attempted. Chemical shifts are approximate (±0·03 p.p.m.). [i] Data have been reported [4] for a 2,3-dichlorobutene; see text. [j] Approximate value estimated from line-width. [k] Data have been recorded at 40 MHz [25] and 60 MHz; [26,27] see text. [l] (6d) and (6e) are the same as (1a) and (1b) (Table 2). [m] Slightly different values have been given by Robinson.[4]

The n.m.r. data required [20–27] for our calculations are in Table 3. Most of the assignments either follow unambiguously from the spectrum or degeneracy or near-degeneracy is apparent in which case coincident chemical shifts are assumed. For data taken from the literature assignments are assumed correct. Kirmse and Kapps [26] These values are low relative to the experimental shifts but indicate δ_2 at low field in accord with the assignment of Kirmse and Kapps.[26] Robinson [4] has reported for 2,3-dichlorobut-1-ene (6f) δ_1 = 5·52 and δ_2 = 5·20 but, by analogy with 2,3-dichloropropene (4f), we prefer the reverse assignment (Table 3). Sup-

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[26] W. Kirmse and M. Kapps, *Chem. Ber.*, 1966, **99**, 2869.

[27] Varian High Resolution N.M.R. Catalog, National Press, 1962, Spectrum 18.

porting evidence can be found in the spectra of 2-chloropropene (3f) and 2-chlorobut-1-ene (5f) where in each case $\delta_1 = \delta_2$. The substitution of the second chlorine into (3f) and (5f) is expected to produce deshielding of δ_2 relative to δ_1 in both systems.

trans- and *cis*-2-Chlorobut-2-ene (3d, 3e) cannot be distinguished by use of either of the available tabulations of σ values. From the data of Matter *et al.* (Table 1) the calculated values are δ_2(3d) = 5·60, δ_1(3e) = 5·61 and with Tobey's values (Table 1) δ_2(3d) = 5·53 and δ_1(3e) = 5·56. Applying the model compound approach,[9] from data for *cis*- and *trans*-1-chloropropene[24] and σ_{Me} values we have δ_2(3d) = 5·12, δ_1(3e) = 5·52. A similar calculation based on *cis*- and *trans*-but-2-ene (3b, 3c) (Table 3) and σ_{Cl} values gives δ_2(3d) = 5·52, δ_1(3e) = 5·59. Neither set of calculated chemical shifts agrees exactly with the experimental values (Table 3) but the trend is the same in each case with δ_1(3e) downfield from δ_2(3d). The only other model compound is 2-chloropropene (3f) but in this case Tobey's method breaks down completely since the calculated values are $\delta_1 = \delta_2$ = 5·55. The relationship between the magnitude of *cisoid* and *transoid* allylic coupling constants is complex[28,29] and these coupling constants are of limited value for structure determinations[29] (however see below). On the other hand, for but-2-enes, the *transoid* homoallylic coupling is consistently greater than the *cisoid* coupling[21,29-31,32] and the larger homoallylic coupling in 3d(J_{13}) relative to 3e(J_{23}) confirms the above assignment.

cis- and *trans*-3-Chloropent-2-ene (5d, 5e) can be assigned by analogy with the butenes (3d, 3e). With *cis*- and *trans*-pent-2-ene (5b, 5c) as model compounds δ_2(5d) = 5·49, δ_1(5e) = 5·51, but this method again fails when applied to 2-chlorobut-1-ene (5f) when the calculated values are δ_2(5d) = δ_1(5e) = 5·56. The assignment of (5d) and (5e) is difficult on the basis of these results but the analogous assignment to the butenes (3d, 3e) is confirmed by the relative magnitudes of the homoallylic coupling constants (Table 3).

From the σ values in Table 1 the predicted shifts for the 1,2-dichlorobut-2-enes (4d, 4e) are δ_2(4d) = 5·94, δ_1(4e) = 5·84. With the 1-chlorobut-2-enes (4b, 4c) as model compounds δ_2(4d) = 5·89, δ_1(4e) = 5·85, and with 2,3-dichloropropene (4f), δ_2(4d) = 6·03, δ_1(4e) = 5·85. All these results suggest the assignment of (4d) and (4e) which has δ_2 (4d) at lower field than δ_1(4e), and this is again consistent with the relative magnitudes of the long range coupling constants (Table 3).

The stereochemistry of all the compounds discussed above has been further confirmed by study of benzene-induced solvent shifts. The general usefulness of solvent shifts in stereochemical investigations is well established[33,34] and some applications to chloro-olefins have been reported.[12,35] For benzene shifts the proton *trans* to the chlorine has a greater shift than the *cis*-protons.[12,35] The benzene solvent shifts in Table 4 support the assignments for the terminal methylene protons in (4f) and (6f), and each of the *cis*–*trans* pairs (3d), (3e), (4d), (4e), (5d), and (5e) show the expected order of shift (*trans* > *cis*) for both the proton and the methyl group, further confirming the usefulness of this method.

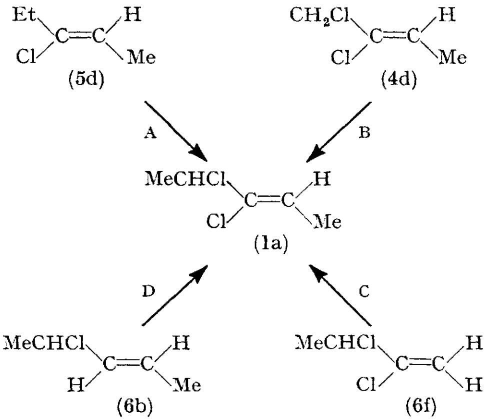
TABLE 4

Solvent shifts[a] [$\Delta = \delta(CDCl_3) - \delta(C_6H_6)$] for some chloro-olefins

Cmpd.[b]	Δ_1 [b]	Δ_2 [b]	Δ_3 [b]	Δ_5 [b]
(3d)[c]	0·16	0·38	0·28	
(3e)[c]	0·15	0·42	0·30	
(3f)[c]	0·11	0·37	0·38	
(4d)	0·42	0·74	0·56	
(4e)	0·50	0·73	0·61	
(4f)	0·39	0·57	0·57	
(5d)	0·13	0·35	0·22	0·18
(5e)	0·12	0·42	0·26	0·14
(5f)	0·14	0·36	0·34	0·30
(6d)[d]	0·36	0·63	0·43	0·30
(6e)[d]	0·38	0·57	0·41	0·25
(6f)	0·42	0·62	0·54	0·36

[a] In p.p.m. [b] Numbering is the same as in Table 3. [c] Very similar data for CCl_4–C_6H_6 shifts are given in ref. 12. [d] (6d) and (6e) are equivalent to (1a) and (1b).

In Scheme 1 the four model compounds differ from (1a) by only one group, including changes in the side chain. Similarly Scheme 2 (not shown) can be drawn up relating the corresponding series of *cis* model compounds to (1b). Substituent constants σ^* have been derived for both the vinyl protons δ_1 or δ_2 and the allylic protons δ_3 for each of the routes A, B, C, or D from a study of closely similar series of compounds. The substituent value σ^*_X is defined as the change in chemical shift of the proton at position X subsequent upon some specified change in the system.



SCHEME 1

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For example, for route A, substitution of an allylic chlorine, a possible parallel model pair is propene (3a) and allyl chloride (4a). From the data for these two compounds (Table 3) the derived substituent constants are $\sigma^*_1 = 0{\cdot}26$, $\sigma^*_2 = 0{\cdot}37$ and $\sigma^*_3 = 2{\cdot}34$. Applying these values to (5d) (Scheme 1, route A) we get for (1a), $\delta_2 = 5{\cdot}84$ and $\delta_3 = 4{\cdot}61$ and to (5e) (Scheme 2, route A) for (1b), $\delta_1 = 5{\cdot}85$ and $\delta_3 = 4{\cdot}63$. Nine other pairs of compounds can be selected from Table 3 where in each case the only difference is the presence or absence of an allylic chlorine. Each pair yields σ^* values for some or all of the positions 1,2, and 3 which in turn yield calculated values for δ_2, δ_3(1a) and δ_1, δ_3(1b). The results of these calculations relating to route A and of similar calculations for routes B, C, and D are collected in Table 5.

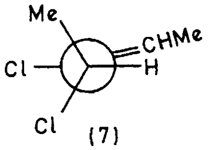
TABLE 5

Calculated chemical shifts for (1a) and (1b)

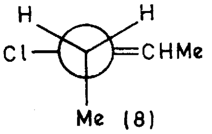
Route	Model pair	δ_1(1b)	δ_3(1b)	δ_2(1a)	δ_3(1a)
A	(3a,4a)	5·85	4·69	5·87	4·68
	(3b,4b)			5·87	4·72
	(3c,4c)	5·85	4·86		
	(3d,4d)			5·99	4·44
	(3e,4e)	5·86	4·57		
	(3f,4f)	5·89	4·40	5·98	4·38
	(5a,6a)	5·83	4·80	5·84	4·78
	(5b,6b)			5·83	4·91
	(5c,6c)	*a*	5·16		
	(5f,6f)	5·80	4·64	5·91	4·62
B	(3a,5a)	5·86	4·60	5·90	5·54
	(3b,5b)			5·95	4·50
	(3c,5c)	5·81	4·69		
	(3d,5d)			5·99	4·44
	(3e,5e)	5·86	4·63		
	(3f,5f)	5·90	4·50	5·99	4·44
	(4a,6a)	5·84	4·71	5·89	4·65
	(4b,6b)			5·91	4·69
	(4c,6c)	*a*	5·01		
	(4f,6f)	5·81	4·74	5·92	4·68
C	(3a,3b)			6·00	4·57
	(3a,3c)	5·90	4·54		
	(3f,3d)			5·91	4·62
	(3f,3e)	5·84	4·57		
	(4a,4b)			6·00	4·62
	(4a,4c)	5·90	4·79		
	(4f,4d)			5·92	4·68
	(4f,4e)	5·81	4·74		
	(5a,5b)			6·03	4·53
	(5a,5c)	5·85	4·63		
	(5f,5d)			5·91	4·62
	(5f,5e)	5·80	4·64		
	(6a,6b)			6·02	4·66
	(6a,6c)	*a*	5·01		
D	(3a,3f)	*a*	5·27	5·88	4·92
	(4a,4f)	*a*	4·98	5·99	4·63
	(5a,5f)	*a*	5·17	5·95	4·82
	(6a,6f)	*a*	5·01	6·02	4·66
	(3b,3d)			5·79	4·97
	(4b,4d)			5·91	4·69
	(5b,5d)			5·83	4·91
	(3c,3e)	*a*	5·30		
	(4c,4e)	*a*	5·01		
	(5c,5e)	*a*	5·18		

[a] Not measured.

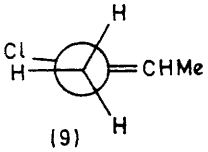
The 44 sets of derived σ^* values give 28 estimates each for the chemical shifts in (1a) and (1b), and the mean values and standard deviations are in Table 2. Several points arise from these calculations. The good agreement between observed and calculated chemical shifts for (1a) strongly supports its assignment as *trans*-3,4-dichloropent-2-ene. For the *cis*-isomer the predicted value for δ_1(1b) is reasonably close to the observed value but the allylic proton shift δ_3 is grossly out. On the basis of predicted allylic proton chemical shift (1a) and (1b) are virtually indistinguishable and only marginal improvement in the calculated values is obtained by omitting all data derived from compounds of series (3), *i.e.* those model compounds most different from (1a) and (1b). However if only route D in Scheme 2 is considered (*i.e.*, with the very similar system, 4-chloropent-2-ene, as model) then the agreement between predicted value, δ_3(1b) = 5·13, and observed value is excellent. The appreciable deshielding of the allylic proton in (1b) probably arises from the close proximity of the *cis*-methyl group. Inspection of a model (*cf.* 7) shows that for the dichloropentenes H(3) is held in an eclipsed position by the other substituents. In the nomenclature of Newsoroff and Sternhell,[28] this corresponds to a dihedral angle of 90° and from the correlation curves of Sternhell[29] the predicted allylic coupling constants are J_{cisoid} *ca.* 0·0 Hz, $J_{transoid}$ *ca.* 0·7 Hz. Good agreement is obtained for the observed *cisoid* coupling J_{23}(6d) 0·3 Hz but the *transoid* coupling J_{13}(6e) 0·2 Hz is low. This may indicate such a severe interaction between the allylic proton H(3) and the *cis*-methyl group that some rotation occurs to give a lower dihedral angle and hence a smaller *transoid* coupling (for $\phi = 75°$ $J_{transoid} =$ *ca.* 0·4 Hz) or may reflect some other factor.



(7)



(8)



(9)

For system (8) the dihedral angles are 60° and 300°. Torsional strain will probably increase these to *ca.* 75° and 315° giving[29] J_{cisoid} *ca.* −0·4 Hz and $J_{transoid}$ 0·0 Hz in agreement with the observed couplings, J_{23}(4d, 5d) and J_{13}(4e, 5e). For the 2-chlorobut-2-enes (9) the dihedral angles of 30°, 150°, and 270° give, from Sternhell's curves,[29] $J_{cisoid} = J_{transoid} =$ *ca.* −1·0 Hz. Similar values obtain for a configuration of type (7). The observed values are J_{23}(3d) = J_{13}(3e) = −1·2 Hz.

This supporting evidence of the allylic coupling constants taken with the solvent-shift studies leads to the conclusion that all of the geometric assignments made on the basis of the somewhat inconclusive data from Tobey's model compound approach, are correct. The extended model compound studies discussed above indicate the limitations of this approach when applied to allylic chemical shifts where other steric factors may play a dominant role.

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