Antimony Halides as Solvents. Part IX.[1] The Dimerisation of *trans*-Stilbene in Molten Antimony Trichloride

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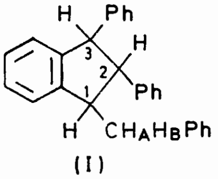
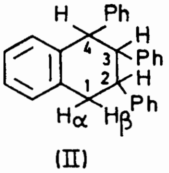
trans-Stilbene forms a mixture of three cyclic dimers in molten antimony trichloride. One of these has an indane structure, and the other two are isomeric tetralin derivatives. The conformations of these products, and of two further isomers of the indane dimer prepared by other methods, have been assigned from their 100 or 220 MHz n.m.r. spectra. A fourth indane ' isomer ', reported by previous workers, is actually a tetraphenylbutane.

In Part I of this series,[2] it was reported that *trans*-stilbene is completely dimerised in molten antimony trichloride. The dimer was similar to that obtained in concentrated sulphuric acid by Brackmann and Plesch,[3] who suggested, on the basis of i.r. spectroscopic evidence, that the major component was 1-benzyl-2,3-diphenylindane (I). This should have four geometrical isomers (all optically active), and a mixture of such isomers would account for the indefinite melting point of the dimers.



(I)

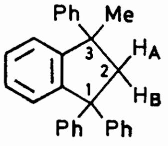


(II)

More recently, Salzwedel *et al.*[4] have dimerised stilbene by γ-irradiation in tin tetrachloride, and have claimed the separation of three of the isomers of (I), which were identified by ^1H n.m.r. spectroscopy. However, no details were given and several of the vicinal coupling constants were extraordinarily small (*ca.* 3 Hz) for an indane.[5] We have, therefore, undertaken the separation of the isomers formed in antimony trichloride and have reappraised their n.m.r. spectra at 100 and 220 MHz. Judging by melting points, we appear to have isolated the same products as those of Salzwedel *et al.*, but we have concluded that only one of them is, in fact, an indane, while the other two are isomers of 2,3,4-triphenyltetralin (II).

In addition, we have repeated the various syntheses of (I) reported by Bergmann,[6] who claimed three further isomers of melting points 115, 143, and 184°. From their n.m.r. spectra, we have confirmed that the first two compounds are indanes (although the second isomer melted sharply at 139°), but have concluded that the 184° compound is actually an isomer of 1,2,3,4-tetraphenylbutane.

For comparison, we have recorded the n.m.r. spectrum of (III), the cyclic dimer formed by 1,1-diphenylethylene in molten antimony trichloride.[7]



(III)

EXPERIMENTAL

All starting materials (B.D.H.) including antimony trichloride were used without further purification.

Dimerisation of trans-*Stilbene*.—The olefin (2 g) was added to molten antimony trichloride (10 g). The resulting solution was maintained at 98° for 2 h and then poured into concentrated hydrochloric acid. The mixture was extracted twice with benzene, and the combined benzene layers were washed with more acid until free of antimony; they were then washed with water until neutral and then dried ($CaCl_2$) and evaporated to yield a brown resinous material, which had a melting transition of 50—70°. We obtained the same material by the ^{60}Co γ-irradiation of *trans*-stilbene in an excess of tin tetrachloride, as described by Salzwedel *et al.*[4] Both products had molecular weights of *ca.* 360 (cryoscopic in benzene), gave a blue fluorescence in u.v. light, and showed identical i.r. and analytical g.l.c. spectra. The best separation was obtained on a 9 ft × $\frac{1}{4}$ in Carbowax 20 M column in nitrogen (40 ml min^{-1}) at 238°. This gave three overlapping peaks, but the poor resolution did not justify a preparative g.l.c. separation.

Column Chromatography.—Samples (1 g) of the resin were chromatographed on Brockman II alumina with benzene–light petroleum (1 : 4) as eluant. Trituration of the eluted oils with ethanol yielded crystalline material which fell into two melting point ranges, 90—100 and 110—115°. Under u.v. light three fluorescent bands remained on the column, but on elution with benzene these gave only small amounts of brown resinous material (m.p. *ca.* 70°). Repeated fractional crystallisation of the crystalline products from propan-1-ol gave the following final fractions, all of which were colourless:

Fraction (1): clusters of needles, 500 mg, m.p. 99° (Found: C, 92·9; H, 6·8%; *M*, 360); fraction (2): prisms, 70 mg, m.p. 146°, separated by hand from the mother liquors of fraction (1) (Found: C, 93·1; H, 6·6%; *M*, 360); fraction (3): needles, 200 mg, m.p. 114° (Found: C, 92·8;

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[1] Part VIII, P. V. Johnson and E. C. Baughan, *J. Chem. Soc.* (*A*), 1971, 2856.

[2] G. B. Porter and E. C. Baughan, *J. Chem. Soc.*, 1958, 744.

[3] P. H. Plesch and D. S. Brackmann, *J. Chem. Soc.*, 1953, 1289.

[4] M. Salzwedel, V. Werner, and D. Schulte-Frohlinde, *Angew. Chem. Internat. Edn.*, 1964, **3**, 803.

[5] Personal communication from Dr. D. Schulte-Frohlinde.

[6] (*a*) E. Bergmann and H. Weiss, *Annalen*, 1930, **480**, 68; (*b*) E. Bergmann, C. Winter, and W. Schreiber, *ibid.*, 1933, **500**, 122.

[7] A. G. Evans, E. A. James, and E. D. Owen, *J. Chem. Soc.*, 1961, 3532.

H, 6·9%; *M*, 360). The analyses of these fractions confirmed the formula $C_{28}H_{24}$ (Calc.: C, 93·3; H, 6·7%; *M*, 360). Molecular weights were obtained from mass spectra. The fragmentation patterns showed no significant differences; in particular they all showed a peak at *m*/*e* 91, corresponding to benzyl. The i.r. spectra were also very similar.

Synthesis of Further Isomers of Compound (I).—Bergmann's methods were used to synthesise two more isomers; the first, melting at 115°, from 2,3-diphenylinden-1-one,[6a] and the second, m.p. 139° (lit., 143° [6b]), by the catalytic *cis*-hydrogenation of 2,3-diphenyl-1-benzylindene [6a] (Found: 115° isomer, C, 93·2; H, 7·0. 139° isomer, C, 92·6; H, 6·0. Calc. for $C_{28}H_{24}$: C, 93·3; H, 6·7%). The latter preparation gave considerable difficulty, which was eventually overcome by the use of a large amount of 5% palladium–charcoal catalyst (equal in weight to the indene).

The third ' isomer ' (m.p. 184°) reported by Bergmann [6b] was also prepared by his methods, which included the reduction of 1,2,3,4-tetraphenylbutadiene. However, analysis corresponded more closely (and not surprisingly) to 1,2,3,4-tetraphenylbutane (Found: C, 92·7; H, 7·3. Calc. for $C_{28}H_{26}$: C, 92·8; H, 7·2%). The 220 MHz n.m.r. spectrum [8] confirmed this revised assignment, with multiplets at $\delta \sim 2{\cdot}5$ (2H), 2·8 (2H), 3·1 (2H), and 6·6—7·2 p.p.m. (20H). As reported by Bergmann, the above reduction also produces a second component, m.p. 99°. The analysis and 220 MHz spectrum [8] show that this is another isomer of 1,2,3,4-tetraphenylbutane [(Found: C, 93·0; H, 7·1%) multiplets at $\delta \sim 2{\cdot}8$ (2H), 3·2 (4H), and 6·7—7·1 p.p.m. (20H)]. In both n.m.r. spectra the low-field aliphatic doublet characteristic of the indanes (Figure 1) is absent, and the ratios of aromatic to aliphatic protons are 20 : 6, compared with 19 : 5 for structure (I). The two compounds are probably the meso and racemic forms, but even at 220 MHz the spectra are too complex to assign configurations by inspection, and we hope to publish a full analysis later.

Dimerisation of 1,1-*Diphenylethylene*.—The same procedure as described above for stilbene yielded 1,1,3-triphenyl-3-methylindane in 95% yield, m.p. 143° (lit.,[9] 143°). The n.m.r. parameters, referred to structure (III), were δ (p.p.m.) CH_3, 1·53; H_A, 3·38; H_B, 3·08; J_{AB} −13·3 Hz; aromatic: aliphatic protons, 9 : 10·9 (required 9 : 11·0).

Analyses and Spectra.—All elemental analyses were performed by the Alfred Bernhardt Microanalytical Laboratory (West Germany). N.m.r. spectra were recorded by the S.R.C. postal service units at Harwell and Runcorn, on Varian HA-100 D and HR-220 instruments respectively, using 5—10% solutions in deuteriochloroform at ambient temperature (38°), with tetramethylsilane as internal reference. Nitro[$^{2}H_{5}$]benzene was used as solvent for variable-temperature measurements, with hexamethyldisilane as reference. Computer analyses were performed at the Atlas Computer Laboratory, Didcot, using 7-spin basic and iterative programmes from the University of East Anglia, and mass spectra were recorded by the S.R.C. unit at Aldermaston.

RESULTS

The n.m.r. spectra for all the isomers of (I) and (II) isolated in this work are given in Figures 1 and 2, and the coupling constants are summarised in Table 1. The assignments were checked wherever possible by spin-decoupling experiments. For the indanes, the 100 MHz spectra were sufficiently first order for the coupling constants J_{12} and

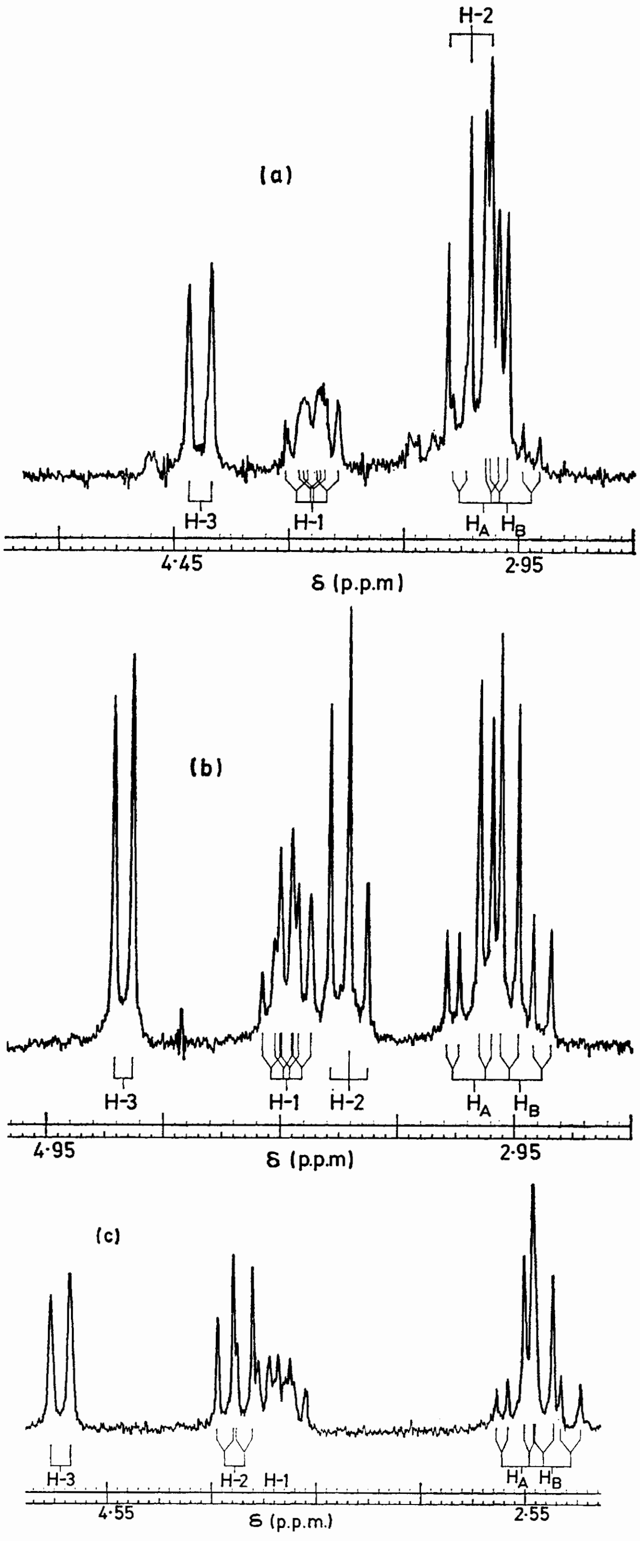

FIGURE 1 N.m.r. spectra of indanes (I) at 100 MHz; (a) 99° isomer, (b) 115° isomer, (c) 139° isomer

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[8] M. Hiscock, M.Phil. Thesis, University of London, 1971.

[9] C. S. Schoepfle and J. D. Ryan, *J. Amer. Chem. Soc.*, 1930, **52**, 4021.

J_{23} to be obtained directly from the 2-H and 3-H multiplets, while the remaining coupling constants were calculated by ABX analyses[10] of the AB multiplets. The X component (1-H) consists of four lines only (the other two having negligible intensity), and these are split into doublets by 2-H in the 99 and 115° isomers. In the 139° form (Figure 1c), however, the signal is of higher order because of its close proximity to the 2-H multiplet. All the results gave good computer simulation without further adjustment.

Table 1

Coupling constants[a] (Hz) between aliphatic protons at 38°

M.p. (°C)	Indanes (I) 99[b]	115	139		Tetralins (II) 114[b]	146[b]
J_{AB}	−13·5	−13·5	−13·0	$J_{\alpha\beta}$	−16·6	−17·0
J_{A1}	5·5	4·9	4·2	$J_{\alpha 2}$	4·1	4·8
J_{B1}	7·5	7·6	8·8	$J_{\beta 2}$	12·0	10·9
J_{12}	9·5	7·8	7·5	J_{23}	11·5	3·5
J_{23}	9·5	7·8	9·0	J_{34}	10·5	2·5
Configurations						
1,2	*trans*	*cis*	*cis*	2,3	*trans*	*cis*
2,3	*trans*	*cis*	*trans*	3,4	*trans*	*trans*?

[a] Limits of error ±0·25 Hz for indanes, ±0·5 Hz for tetralins. [b] Obtained by dimerisation of stilbene in molten $SbCl_3$.

It was necessary to record the spectra of the 114 and 146° isomers at 220 MHz, because at 100 MHz they were either broad and featureless or deceptively simple. Salzwedel *et al.*[5] were thus led by inadequate information at a lower frequency to assume indane structures for these isomers. However, we find that the coupling constants (Table 1) are entirely different from those in the other isomers, and correspond instead to tetralin structures. For example, the large geminal coupling constants, $J_{\alpha\beta}$, are characteristic of endocyclic methylene protons in a six-membered ring,[11,12] rather than an exocyclic group, for which $|J| = 12$—14 Hz only. In addition, similar vicinal coupling constants (J_{aa} 10 and J_{ae} 5 Hz) have been reported for other aryl substituted tetralins.[13,14] The spectrum of the 146° isomer (Figure 2b) shows a similar pattern to those of the indanes (Figure 1) and was analysed in the same way. On the other hand the spectrum of the 114° isomer required computer analysis, and the theoretical ' stick ' plot after six iterations is also shown in Figure 2a.

DISCUSSION

Conformation of Indanes.—Figure 3 shows the conformations which correspond to the vicinal coupling constants J_{12} and J_{23} in Table 1. These assignments have been deduced from the empirical treatment of Pachler *et al.*,[15] which allows for the effect of substituent electronegativities on the Karplus equation. (The 1,2-*cis*-configuration in the 139° isomer also agrees with its mode of synthesis.) Dreiding models have been used to estimate the three interproton dihedral angles possible in a cyclopentene ring, and the corresponding theoretical coupling constants are compared with the observed values in Table 2. The required electronegativity values were assumed[16] to be H = 2·10, C (sp^3 hybridised) = 2·50, and Ph = 2·75. The agreement is close and of the

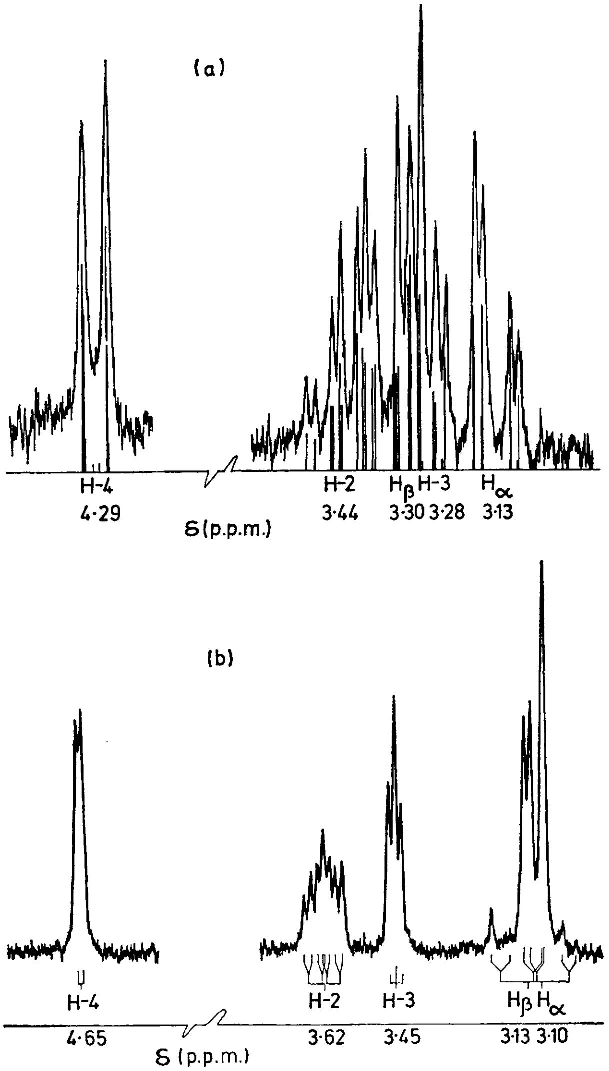

Figure 2 N.m.r. spectra of tetralins (II) at 220 MHz; (a) 114° isomer, (b) 146° isomer

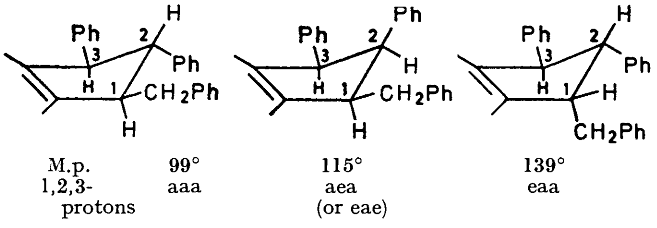

Figure 3 Conformation of indanes

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[10] R. H. Bible, ' Interpretation of N.M.R. Spectroscopy,' Plenum Press, New York, 1965, p. 87.

[11] R. Wallace, A. L. Porte, and R. Hodges, *J. Chem. Soc.*, 1963, 1445.

[12] G. C. Brophy, D. J. Collins, J. T. Hobbs, and S. Sternhell, *Austral. J. Chem.*, 1970, **23**, 1587.

[13] W. L. Bencze, L. I. Barsky, R. W. J. Carney, A. A. Renzi, and G. Destevens, *J. Medicin. Chem.*, 1967, **10**, 138.

[14] J. W. Clark-Lewis and V. Nair, *Austral. J. Chem.*, 1967, **20**, 2137.

[15] K. G. R. Pachler, J. P. Tollenaere, and P. L. Wessels, *Tetrahedron*, 1969, **25**, 5255.

[16] J. R. Cavanaugh and B. P. Dailey, *J. Chem. Phys.*, 1961, **34**, 1102.

same degree as that shown by related indan-1-ols.[17] In the case of the 99 and 139° isomers, the conformers shown in Figure 3 must predominate, because the alternative conformations (eee and aee respectively) would contain 2,3-dihedral angles of 90°, for which the coupling constants would be very small. No such choice can be made for the 115° isomer on the basis of coupling constants, but models show that the form shown in Figure 3 is least crowded.

TABLE 2

Vicinal coupling constants in the cyclopentene ring

Proton configuration[a]		Dihedral angle[b]	Coupling constant (Hz)		
			Theor.[c]		Obs.
			1,2	2,3	
cis	ae	30°	8·3	8·1	~7·8
trans	ee	90	0·4	0·1	
	aa	150	10·0	9·8	~9·5

[a] a = Pseudo-axial, e = pseudo-equatorial. [b] From Dreiding models. [c] Using method of ref. 15.

The chemical shifts (Figure 1) are also consistent with the assigned conformations. Thus, 1-H, 2-H, and 3-H appear at higher field strengths in the all-*trans*- (Figure 1a) than in the all-*cis*-isomer (Figure 1b), because in the former these protons are shielded by *cis*-phenyl or -benzyl groups, while in the latter they are *cis* to each other.

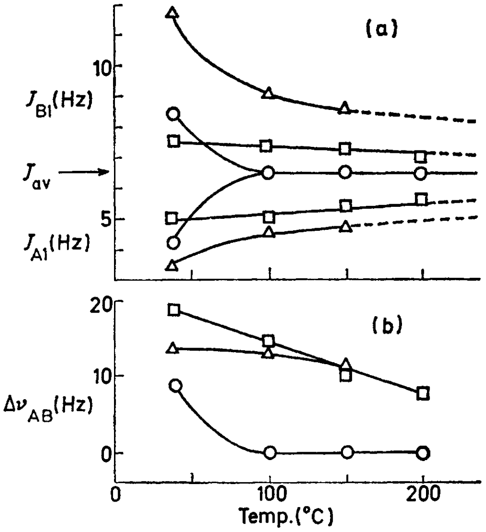

FIGURE 4 Temperature dependence of methylene proton signals in indane spectra; ○ 99° isomer. □ 115° isomer. △ 139° isomer

The same set of conformers has been deduced for the dimers of *trans*-β-methylstyrene [8] and various propenylphenyl ethers.[18] In no case has the 1,2-*trans*-2,3-*cis*-isomer been isolated. We hope to extend our investigations to *cis*-stilbene, in order to see whether the stereochemistry of the monomer influences that of the dimers.

We have further studied the non-equivalent methylene protons by recording the indane spectra at various temperatures in nitro[$^2H_5$]benzene. Figure 4 shows the temperature dependence of J_{A1}, J_{B1}, and $\Delta\nu_{AB}$, the difference in chemical shift between the AB protons. These parameters were calculated by ABX analyses [10] in which the limits of error were ±0·25 Hz. The values for J_{A1} and J_{B1} at 38° differ from those in Table 1 because of the change in solvent. The highest possible temperature for the HA-100 D probe was 200°, and the 139° isomer was unstable above 150°. As the temperature increases, both coupling constants appear to be converging to a common value of *ca.* 6·5 Hz for all three isomers, while $\Delta\nu_{AB}$ decreases (at different rates). One possible explanation for this behaviour is that the rotamer populations are becoming more equal.[19] If this is so, the rotamer populations in the 99° isomer are equal above 100°, and any intrinsic non-equivalence contribution [19] is undetectable. Identical results have been obtained for a related series of indanols [17] whenever there is a *trans*-relationship between the 1-benzyl group and the 2-substituent, as in 99° isomer. Dreiding models show that this isomer has the lowest amount of non-bonded interaction among the conformations in Figure 3, and should therefore approach equal rotamer populations at a lower temperature. Moreover, the average vicinal coupling constant for equally populated rotamers in substituted ethanes can be calculated from the equation [20] $J_{av} = 18—0{\cdot}8\ \Sigma E$, where E = electronegativity of any substituent. Using the electronegativities specified above, the theoretical value for J_{A1} or J_{B1} in these indanes is 6·6 Hz, which agrees closely with J_{av} for the 99° isomer.

Alternatively, the convergence of coupling constants and shifts could be the result of changes in the populations of ring conformations. Such changes were detectable for the 99 and 139° isomers, because in the variable-temperature measurements the spacing J_{23} of the low-field doublet decreased slightly (99° isomer, 9·8—8·8 Hz; 139° isomer, 10·0—8·5 Hz; temperature range as in Figure 4). J_{23} was constant for the 115° isomer (8·0 Hz), but this is not diagnostic because it should be the same for both conformers. It is, however, difficult to predict the sensitivity of $\Delta\nu_{AB}$ to changes in ring conformation, and in view of the behaviour of the 99° isomer it is probable that rotamer populations give the major contribution.

Tetralins.—The results of a conformational analysis of the tetralin data are shown in Figure 5, which is based on a pseudo-chair conformation [21] for the cyclohexene ring. As in the case of the indanes, we have used Dreiding models and the treatment of Pachler *et al.*[15]

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[17] M. Hiscock and G. B. Porter, *J. Chem. Soc.* (*B*), 1971, 1631.

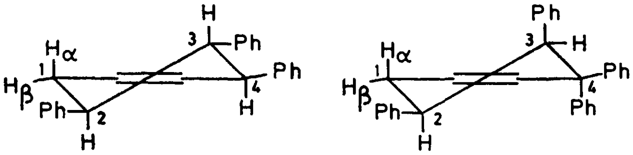
[18] J. MacMillan, I. L. Martin, and D. J. Morris, *Tetrahedron*, 1969, **25**, 905.

[19] L. M. Jackman and S. Sternhell, ' Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' Pergamon, Oxford, 1969, 2nd edn., p. 374.

[20] R. J. Abraham and K. G. R. Pachler, *Mol. Phys.*, 1963, **1**, 165.

[21] H. Peters, R. A. Archer, and H. S. Mosher, *J. Org. Chem.*, 1967, **32**, 1382.

to predict coupling constants, and these are compared with the observed values in Table 3. Of the eight possible conformations of triphenyltetralin, only those shown in Figure 5 agree with the observed n.m.r. data.



M.p. 114° 146°
2,3,4-protons aaa aee? (or aea)

FIGURE 5 Conformation of tetralins

There is, however, some ambiguity in the configuration of the C-4 proton in the 146° isomer. Both axial and equatorial positions would give a dihedral angle of *ca.* 60° with the C-3 proton, and the chemical shift relationships are too complex in these structures to be of any assistance.

Several effects may account for the discrepancies between observed and calculated coupling constants (Table 3) for both the *cis*- and *trans*-configurations.

TABLE 3

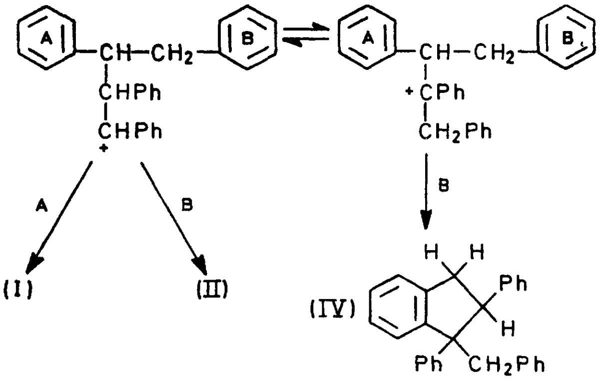
Vicinal coupling constants (Hz) in the cyclohexene ring

Proton configuration		Dihedral angle	1,2		2,3		3,4	
			Calc.^{a}	Obs.	Calc.^{a}	Obs.	Calc.^{a}	Obs.
cis	ae	60°	3·1	4—5^{b}	2·8	3·5^{b}	2·6	2·8^{c}
trans	ee							
	aa	180	13·5	11—12	13·1	11·5	12·8	10·5

^{a} Using method in ref. 15. ^{b} Assigned to ae protons (see Figure 5). ^{c} Assigned to ee protons.

(1) The dihedral angles from which the coupling constants are calculated have been assigned from a consideration of Dreiding models, and the true angles may well be different because of interactions between the ring substituents. (2) The observed lower values for J_{trans} may be due to significant amounts of the di-equatorial conformer present in an equilibrium mixture with the diaxial conformer. (3) The Pachler treatment does not take into account the angular dependence of the electronegativity effect on vicinal coupling constants as shown by Bhacca and Williams.[22] These authors obtained values of 3—5 Hz for J_{ae} depending on the relative orientations of the electronegative group with respect to the vicinal protons. Within the above limitations, we conclude that the observed and calculated values are in fair agreement.

Mechanism of Dimerisation.—The polymerisation of arylolefins in the presence of acid catalysts has been extensively reviewed.[23] When a Lewis acid catalyst is used, the presence of a protonic ' co-catalyst ' is essential. In our samples of antimony trichloride, this was probably water, since no rigorous precautions were taken to exclude moisture. Our results show that the dimer cation formed from stilbene cyclises in *two* ways by attack of the positive centre on ring A or ring B. Tetralin derivatives have recently been obtained by the dimerisation of 1,2,2-trimethylstyrene,[12] but a more complex reaction scheme was invoked in which the 1-methyl group becomes part of the cyclohexene ring.



It should also be possible for the dimer cation to isomerise by hydride-ion shift to a more stable tertiary carbonium ion, which could cyclise to the indane (IV). However, this possesses both endo- and exo-cyclic methylene groups, and there was no indication of such a structure among our products.

The apparent absence of butene formation, from both stilbene and 1,1-diphenylethylene, may be due to the stabilising effect of the solvent $SbCl_3$ on the dimer cation,[7] which would allow time for the slow but irreversible cyclisation step to terminate the reaction. The absence of higher polymers in the dimer mixtures may be due to the steric effect of the bulky phenyl groups, which would inhibit chain propagation.[24] In a trial experiment we found that tetraphenylethylene is recovered unchanged from antimony trichloride after several hours. Hence the carbonium ion formed from this olefin must be so inactivated by steric hindrance (and delocalisation of the positive charge) that even dimerisation is unfavourable.

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[22] N. S. Bhacca and D. H. Williams, *J. Amer. Chem. Soc.*, 1964, **86**, 2742.

[23] P. H. Plesch, ' The Chemistry of Cationic Polymerisation,' Pergamon, Oxford, 1963, p. 306.

[24] S. Ang, ' Encyclopedia of Polymer Science and Technology,' Interscience, New York, 1966, **5**, 121.