Tetrahedron. Vol. 26, pp. 1827 to 1837. Pergamon Press 1970. Printed in Great Britain

STEREOCHEMISTRY OF PERHYDROTRIPHENYLENE—I
SOME REMARKS ON STRUCTURE AND REACTIVITY

M. FARINA* and G. AUDISIO†

(*Received in the UK* 15 *November* 1969; *Accepted for publication* 15 *December* 1969)

Abstract—The stereochemistry of perhydrotriphenylene is discussed and compared with that of inositols, both with regard to the number of isomers and to their chirality. Among the ten isomers (six of which are chirals) particular attention is focused on the *anti-trans-anti-trans-anti-trans* isomer (I), the synthesis, structure, physical properties and reactivity of which are described in detail. The synthesis and structure of perhydrotriphenylen-2-carboxylic acid (XV), with the carboxyl in equatorial position, is discussed. Attempts to obtain other compounds with the same structure are also mentioned.

OUR interest in the chemistry of perhydrotriphenylene arises from the unusual stereochemical and crystallographic properties of one of its stereoisomers[1,2] *Anti-trans-anti-trans-anti-trans*-Perhydrotriphenylene has a highly symmetrical rigid structure (point group D_3) and exhibits the interesting property of forming crystalline inclusion compounds with a number of linear molecules.

Until 1963 the only reference to perhydrotriphenylene concerns the synthesis which leads to a product with an undefined structure.[3] The first unequivocal synthesis of the *anti-trans-anti-trans-anti-trans* stereoisomer was carried out a few years ago,[1] but recently, we resolved this stereoisomer into optical antipodes.[4] A further isomer, *syn-trans-anti-trans-anti-cis*, was isolated and characterized;[5] and the *anti-trans-anti-cis-anti-cis* isomer was identified in the stereoisomeric mixture.

The detailed study of the crystal structure of perhydrotriphenylene and of its inclusion compounds has been published,[6] as well as a conformational analysis of the included molecules.[7] In this paper we wish to give details of the stereochemical properties and of the reactivity of these compounds.

Number and shape of the stereoisomers

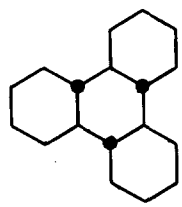
Configurational analysis of perhydrotriphenylene, $C_{18}H_{30}$, shows the existence of ten stereoisomers; there are six enantiometic pairs and four *meso*-forms (Scheme 1). Owing to the presence of cyclic substituents, the six C—C bonds of the central ring are divided into two classes: three of them are *endo* (shared by two cycles) and three *exo*. According to common usage, we apply the *cis-trans* nomenclature (shortened in *C* and *T*) to the former and the *syn-anti* (*S* and *A*) to the latter.

The complex stereochemistry of perhydrotriphenylene as compared with other hexasubstituted cyclohexanes, such as inositol, is evident. There are eight isomers and only one can be resolved into antipodes (Scheme 2). The increased number of stereoisomers is directly connected with the presence of cyclic substituents. Examination of the planar formulas in Schemes 1 and 2 reveals that isomers III and V arise from the same monocyclic structure, that of α-inositol, whereas both isomers VIII and IX

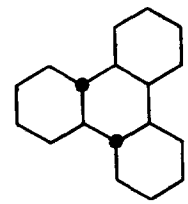
* Istituto di Chimica Industriale del Politecnico, Milano, Italy.
† Istituto di Chimica delle Macromolecole del Consiglio Nazionale delle Richerche, Milano, Italy.

SCHEME 1

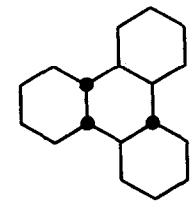
A RACEMIC



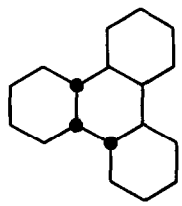
I *ATATAT*



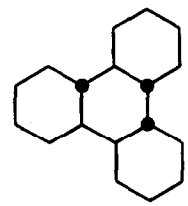
II *STATAC*



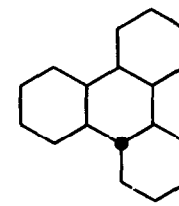
III *ATACAC*



IV *STSCAC*

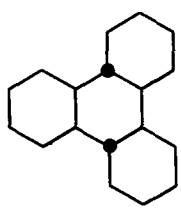


V *STSTAT*

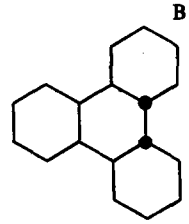


VI *STACSC*

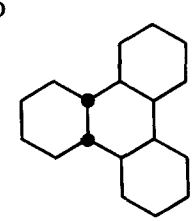
B MESO



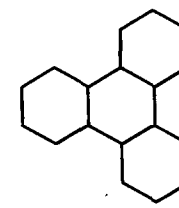
VII *STACAT*



VIII *STSCST*



IX *SCACAC*

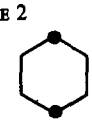


X *SCSCSC*

correspond to *allo*-inositol (or η-inositol). It is easily shown that the absence of mirror planes passing through the atoms in the monocyclic planar structure is a necessary condition for the existence of such duplication.

SCHEME 2

cis (ι) meso → X meso



muco (γ) meso → VII meso

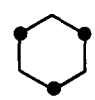
epi (θ) meso → VI racemic

neo (ε) meso → IV racemic

allo (η) meso → VIII meso, IX meso

dl (α) racemic → III racemic, V racemic

myo (δ) meso → II racemic

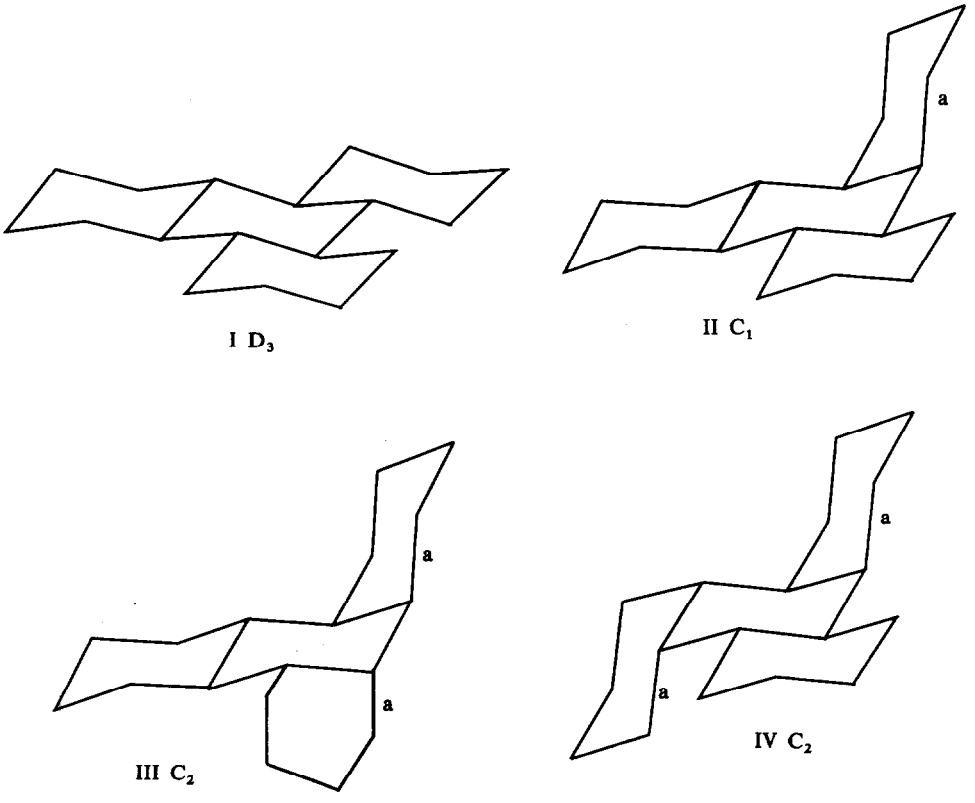


scyllo (β) meso → I racemic

Also, the increase in the number of optically active forms depends on the presence of cyclic substituents: these prevent the existence of the inversion center and of mirror planes passing through the atoms and allow only those planes passing midway between the bonds. Consequently, only the isomers of perhydrotriphenylene corresponding to the γ, η and *cis*-inositol (respectively VII, VIII and IX, X) are *meso* forms, at least from the configurational point of view.

On the basis of energetic considerations, not all these stereoisomers seem to have a reasonable stability. Only four of them (I, II, III and IV) can exist in chair conformation without any 1,3-di-axial interaction (Scheme 3). Among them, isomer I (or *A T A T A T*) is particularly noticeable as it possesses a completely equatorial conformation and a high symmetry (point group D_3). Isomers II, III and IV possess one or two C—C axial bonds and have an energy higher than that of I.[5]

SCHEME 3



As for the other isomers, neither the conformation nor the energy can be foreseen in a similar manner; contrasting factors contribute to their determination, e.g., the presence of boat conformations and of 1,3-di-axial interactions, the relative magnitude of which is not sufficiently known. Any chair conformation of the central ring is forbidden in V as it would cause *trans*-di-axial junctions: a "skew-boat" structure, too, should have a high energy owing to the presence of extraanular eclipsed contacts.

VII and VIII probably have the central ring and one of the side rings in boat conformation, and they could be true *meso* forms (idealized symmetry group C_s). No low-energy molecular model can be built for VI, IX and X. As for the last two, the symmetry of the more likely models belongs to the C_1 group. In this case, IX and X should exist in two more or less rigid enantiomeric conformations.

Synthesis and identification of the stereoisomers of perhydrotriphenylene

In spite of what has been repeatedly stated,[3, 8] perhydrotriphenylene can be obtained by catalytic hydrogenation from aromatic compounds having the same skeleton, in particular from dodecahydrotriphenylene XI.[1] The latter may be obtained either from cyclohexanone[8, 9] or by reaction of 1,4-dichlorobutane with benzene[10] or tetraline.[11]

The hydrogenation conditions (i.e., temperature, choice of catalyst and solvent and the reaction time) are particularly critical. The best catalyst is palladium on coal, whereas Ni Raney is far less effective. Also the solvent plays an important role: the reaction gives high yields in the presence of saturated hydrocarbons, whereas it does not proceed in the presence of methanol and ethanol.

The mixture obtained by hydrogenation consists of four components, called α, β, γ and δ, according to increasing retention times in GLC. β corresponds to isomer I, whereas γ was identified as the *syn-trans-anti-trans-anti-cis* isomer (II) on the basis of equilibration experiments.[5] The equilibrium constant of reaction $\gamma \rightleftarrows \beta$ was determined in the presence of palladium ($K = 1{\cdot}95 \pm 0{\cdot}20$ at 287°). Its value agrees with that calculated for equilibrium II $\rightleftarrows$ I on the basis of conformation and symmetry considerations.

Isomer II was isolated by GLC and characterized by spectroscopic methods.[5] In an analogous manner, component α was tentatively identified as the *anti-trans-anti-cis-anti-cis* isomer (III).[5]

The results obtained from a series of hydrogenations terminated at different times are reported in Table 1. The data and the value of the ratios γ/β and α/γ show that β is derived from successive epimerization of other stereoisomers. Among the compounds we have detected and identified, γ clearly is formed before β; and α probably forms before γ. This behaviour agrees with a *cis* stereochemistry of the primary process, followed by stepwise inversions at tertiary carbons. The first steps of this epimerization however (e.g. from VIII–X to III or IV) are very rapid; some small additional peaks are observed in the gas-chromatograms only when hydrogenation is not complete and XI is still present in the reaction mixture.

Stereoisomer I can easily be isolated from the other low-melting isomers as a crystalline inclusion compound containing n-heptane, from which it can be obtained in the pure state by heating under vacuum followed by sublimation or by crystallization from methyl ethyl ketone.

The structure of the high-melting isomer was at first assigned on the basis of the physical properties and by the method of synthesis. Its high m.p. and the high yields obtained by catalytic hydrogenation suggest that it possesses a highly symmetrical and stable structure. These facts are in agreement with structure I which has a symmetry number of 6 and a fully equatorial conformation.

The X-ray determination of the crystal structure of the inclusion compound between I and n-heptane confirmed the formula proposed.[2, 6]

A peculiar property of I is its tendency to polymorphism. We succeeded in isolating two crystalline forms of the chemically pure compound and at least four different classes of inclusion compounds with several substances.[6]

In the pure state (monoclinic form, space group $P2_1/a$) I melts at 128°. The m.ps of the inclusion compounds with linear hydrocarbons (hexagonal form, space group $P6_3/m$) increase with the length of the included molecule. For instance, the adduct with n-octacosan shows a congruent melting at 160°. The m.ps reach a limiting value beyond 180° for the adducts containing linear macromolecules, such as polyethylene and *trans*-1,4 polybutadiene.[2, 6]

The IR spectrum of I in the region between 670 and 1400 cm^{-1} is characterized by the following bands: 834 s, 896 s, 918 m, 960 w, 978 m, 1050 m, 1070 w, 1105 w, 1130 w, 1170 m, 1210 s, 1265 w, 1288 m, 1294 w, 1328 w, 1340 w, 1352 s, 1365 w. The sharp bands between 800 and 1000 cm^{-1} are very useful for its characterization. The transparency of I in the region between 700 and 750 cm^{-1} allows accurate analyses of the inclusion compounds with linear hydrocarbons, using the characteristic rocking band of the methylenic groups of aliphatic chains. The absence of bands around 1000 cm^{-1} allows the analysis of mixtures of I and II; the latter shows absorption bands of medium intensity at 988 and 1008 cm^{-1}.[5] The mass spectrum of I is characterized by a very high molecular peak at *m/e* 246. The most important fragmentation peak is placed at 189 (M-57) and is typical of this series of compounds.

Owing to its molecular symmetry, the 30 H-atoms of I can be grouped in 5 classes, which are respectively called H*t* (tertiary), H1*a*, H1*e*, H2*a* and H2*e* (*a* and *e* mean axial and equatorial). The 100 mc spectrum of I (Fig. 1a) reveals the presence of four groups of bands of relative intensity 1:1:1:2, which are attributed as follows: 1·95 δ H2*e*, 1·71 δ H1*e*, 1·14 δ H2*a*, 0·68 δ H1*a* + H*t* (in CCl_4, internal reference TMS). The bands were assigned by spin decoupling and by comparison with the spectrum of trimethylcyclohexane.[12]

Chemical behaviour of perhydrotriphenylene

The various isomers of perhydrotriphenylene are very sensitive to the action of hydrogenation and isomerization catalysts. In the presence of Pd/C and in the open

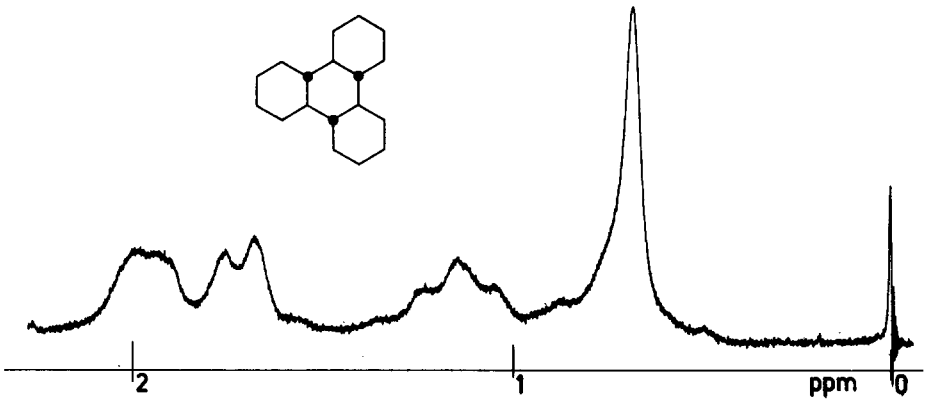


FIG. 1a NMR spectrum of perhydrotriphenylene (I)

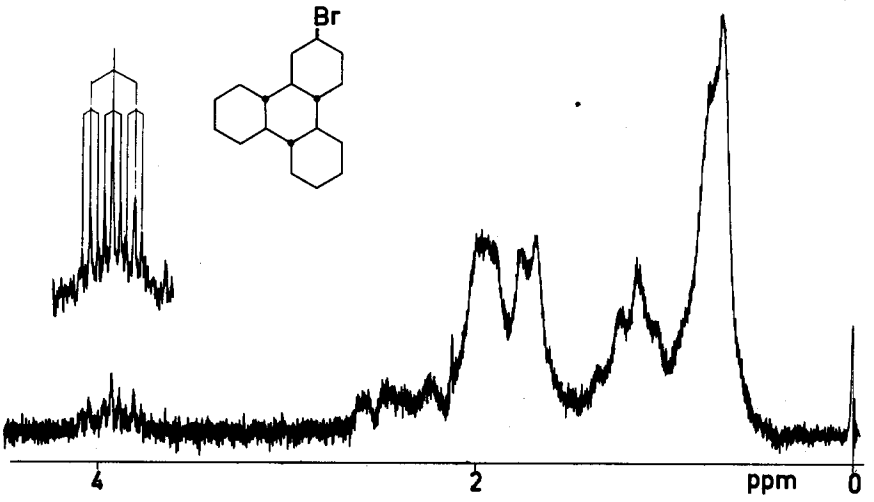
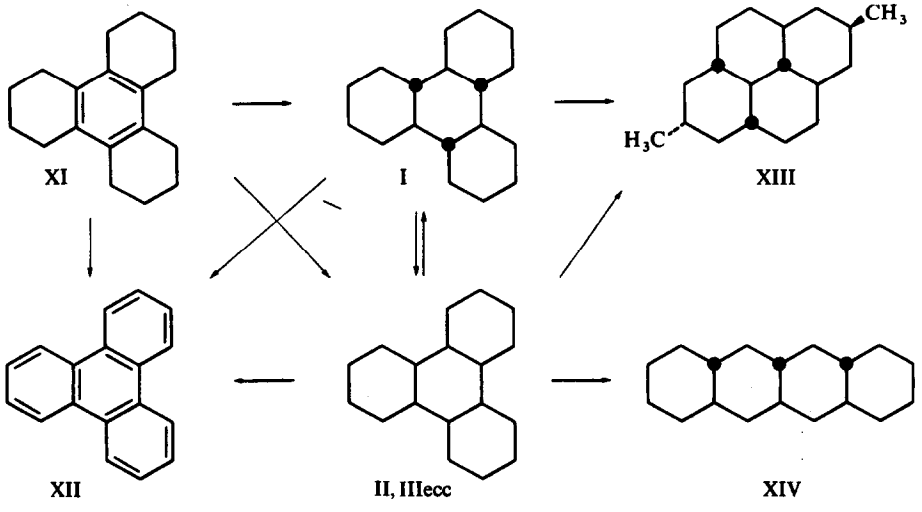


FIG. 1b NMR spectrum of 2-bromo-perhydrotriphenylene. This is the stereoisomer with bromine in equatorial position (XVI)

air, both I and the mixture of isomers II, III, etc., are quantitatively transformed at 250–300° into triphenylene XII (Scheme 4). Under hydrogen pressure, on the contrary, an epimerization of the various stereoisomers takes place until equilibrium is reached.[5]

In the presence of acid isomerization catalysts, such as $AlCl_3$, the reaction is more complex and gives rise to tetracyclic compounds with different skeletons. Depending on the conditions, either the equatorial 2,7-dimethylperhydropyrene (XIII)[13] or the equatorial isomer of perhydronaphthacene (XIV)[14] is obtained as the main product. A more complete study of the isomerization of perhydrotriphenylene in the presence of Friedel–Crafts catalysts will be published in another paper.

SCHEME 4



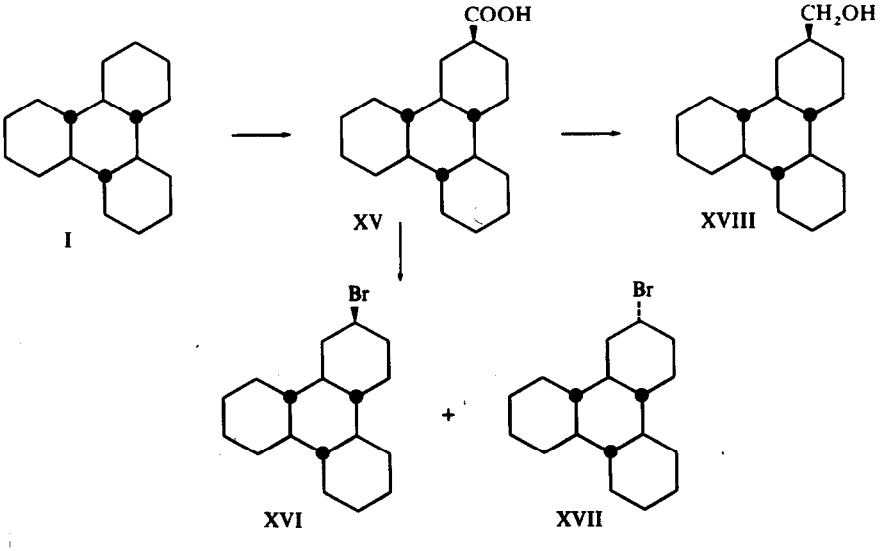
The chemical behaviour of stereoisomer I was studied in more detail. It is inert toward oxidants, such as CrO_3 in boiling acetic acid and $KMnO_4$ in acetone and in acetic acid. No appreciable amounts of ketonic or alcoholic compound have been isolated in these reactions. I is inert also toward iodine or N-bromosuccinimide in the presence of peroxides; *vice-versa* it undergoes a slow aromatization to triphenylene by the action of iodine in the presence of UV light.

Bromine in the presence of BF_3 etherate reacts violently with I with evolution of HBr; the molecule undergoes aromatization and extensive bromination. Depending on the conditions (temperature, excess of bromine, amount of BF_3) the products have a variable composition, e.g. $C_{18}H_8Br_4$ or $C_{18}H_6Br_6$.

Chlorocarbonylation by oxalyl chloride is the best method for the introduction of a functional group into the molecule of perhydrotriphenylene. It is known that oxalyl chloride reacts with saturated cyclic hydrocarbons, such as cyclohexane, in the presence of peroxides or UV light, with production of acyl chloride.[15] This reaction takes place with low conversion; in the presence of benzoil peroxide in boiling CCl_4[4] —the conversion being about 20% after 60 hr whereas by irradiation with a mercury lamp equipped with a Pyrex filter and under a slight chlorine stream[16] it rises to 30–35% after 8 hr only. Perhydrotriphenylene carboxylic acid is obtained in 40% yield, m.p. 221°; its elemental analysis and equivalent weight are consistent with the formula.

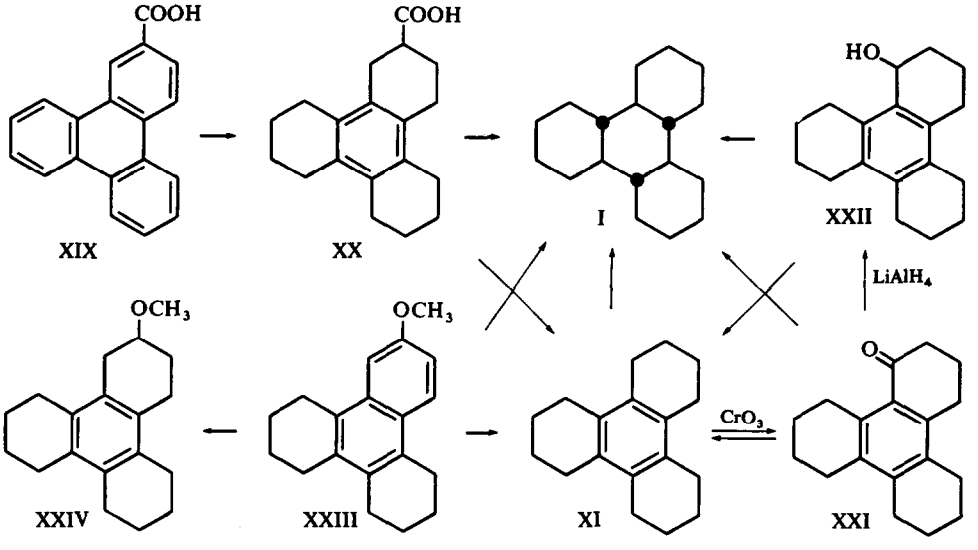
By the Hunsdiecker reaction (Scheme 5), XV is converted (55%) into a mixture of two bromides in a 1:1 ratio, and the structures determined by spectroscopic methods. One of them (XVI), obtained in the pure state by fractional crystallization, has a complex signal in its NMR spectrum interpreted as a triplet of triplets centred at 3·97 δ and with coupling constants of 13 and 4 c/s (area 1/29; Fig. 1b). This signal must be attributed to a CHBr group in position 2 with hydrogen in an axial position, because of the odd multiplicity and of the high value of one of the vicinal coupling constants, which is typical of the axial-axial couplings.

SCHEME 5



The second isomer (XVII) obtained in a less pure form shows a poorly resolved multiplet centred at 4·66 δ, which is also attributed to the CHBr group. The odd multiplicity supports position 2 and the small coupling constants (about 3 c/s) indicate that the proton is in equatorial position.

SCHEME 6



These conclusions modify the previous tentative assignment of the structure of the acid,[4] but still leave uncertain the stereochemical problem, because of the non stereospecificity of the Hunsdiecker reaction. The equatorial position of the carboxyl was determined by examining the NMR spectrum of perhydrotriphenylenilcarbinol (XVIII) obtained from the acid, by esterification and reduction with LAH. The signal from the two hydrogens of the CH_2OH group consists of a doublet centred at 3·36 δ coupled with a proton situated at 1·37 δ, very near to the resonance frequency of the

TABLE 1. HYDROGENATION OF DODECAHYDROTRIPHENYLENE (TEMP: 280 ±5°; press H_2: 200 atm; Catalyst: 10% Pd/C; solvent: n-heptane)

	Run A	Run B	Run C	Run D	Run E
Catalyst % by wt	1	5	5	5	5
Time (hr)	7	7	12	22	100
Conversion %	14	64·5	98	100	100
α %	19·3	16·4	9·4	4·2	2·8
β %	12·1	22·9	39·9	57·0	63·0
γ %	45·7	51·8	48·6	38·3	33·2
δ %	2·9	2·2	2·1	0·5	0·4
other isomers %	20·0	6·7	0	0	0
γ/β	3·78	2·26	1·22	0·67	0·52
α/γ	0·42	0·32	0·193	0·110	0·084

2 axial hydrogen in I. By oxidation with chromic anhydride, XVIII is converted again into the acid XV, m.p. 221.

An attempt to synthesize the same acid XV from triphenylene, by acylation, oxidation and subsequent hydrogenation was unsuccessful; the dodecahydrotriphenylene-2-carboxylic acid (XX) is easily obtained, but the subsequent hydrogenation to the perhydro compound was accompanied by hydrogenolysis of the carboxylic group (Scheme 6, Table 2a). The same phenomenon occurs when hydrogenating aromatic compounds containing functional groups, such as dodecahydrotriphenylen-1-one (XXI), dodecahydrotriphenylen-1-ol (XXII), 2-methoxyoctahydrotriphenylene (XXIII). This behaviour must be attributed to the particular difficulty in hydrogenating the central aromatic ring, which is common to many polysubstituted benzenes; the drastic conditions required for hydrogenation lead to the hydrogenolysis of the functional group at the same time.

TABLE 2. HYDROGENATION OF COMPOUNDS WITH TRIPHENYLIC STRUCTURE
(Catalyst: at 10% Pd/C)

Starting compounds	Solvent	Temp °C	P(atm)	Products
XIX	heptane	200	90	XX
XIX	heptane	300	185	I
XX	heptane	250	90	I
XX-sodium salt	water	340	210	I
XXI	heptane or EtOH	110	65	XI
XXI-oxime	EtOH	100	70	XI
XXII	heptane	300	100	I
XXII	EtOH	300	100	XI
XXIII	heptane	150	50	XXIV + XI
XXIII	heptane	200	80	XI
XXIII	heptane	300	100–200	I

EXPERIMENTAL

The IR spectra were recorded on a Perkin–Elmer 221 spectrophotometer. The NMR spectra were run on a Varian HA 100 using TMS as an internal standard. The chemical shifts are given in δ units from TMS and taken as positive in the direction of decreasing magnetic field. Mass spectra were recorded on a Hitachi–Perkin–Elmer RMU 6 D single focus spectrometer, equipped with an all glass heated inlet system, ionization potential 70 ev. GLC were carried out by a F & M 5750 instrument using Apiezon L columns, 3·6 m long, at 250°. M.ps, determined on a hot stage microscope, are uncorrected.

Perhydrotriphenylene (I). The procedure adopted is described in Ref. 5. A detailed analysis of the hydrogenation of XI is shown in Table 1.

Perhydrotriphenylen-2-carboxylic acid (XV). The reaction was carried out in a photochemical reactor equipped with a high-pressure immersion UV lamp (Philips HPK 125 W), water cooled (55°) and with a Pyrex filter.

The boiling soln of I (217 g; 0·88 moles), CCl_4 (700 ml) and $(COCl)_2$ (50 ml; 0·71 moles) was irradiated under a slight Cl_2 stream for 8 hr. Part of unreacted I precipitated in the cold. The filtered soln was concentrated, then MeOH was added to make the remaining I insoluble and to form the methyl ester. After refluxing for 2 hr, the reaction product was cooled and filtered. 170 g of I were recovered. The soln was evaporated at reduced press. 20% KOH (200 ml) was added to the residual oil. Stirring was continued for 24 hr at 90–100°. The cold alkaline suspension was washed with ether heated and acidified with conc HCl (50 ml). The precipitated acid was recrystallized from 1:1 toluene–acetone (23 g), m.p. 221–223°, yield based on reacted I: 41·5%. (Found: C, 78·52; H, 10·51. $C_{19}H_{30}O_2$ requires: C, 78·57; H, 10·41%). The mass

spectrum of the methyl ester, m.p. 120°, shows main peaks at *m/e* 304 (M), 289 (M-15), 286 (M-18), 272 (M-32), 244, 203, 189.

2-Bromoperhydrotriphenylene (XVI *and* XVII). Compound XV (11 g) dissolved in N 0·1 KOH (500 ml) reacted with $AgNO_3$ aq (7 g). The Ag salt was washed with acetone and dried (14·5 g). Br_2 (2·2 ml) in hexane (15 ml) was slowly added to this salt suspended in anhydrous n-hexane (50 ml) under N_2 atm. The reaction was maintained at −5° for 7 hr, at room temp for 2 hr and refluxed for 1 hr. Toluene (100 ml) was added; AgBr was filtered off and the soln was concentrated until precipitation of unreacted XV (1·6 g). With further concentration, 5·7 g of the mixture of the two bromo derivatives was obtained, yield 53%. After three crystallizations from acetone–chloroform (1:1), XVI was obtained in the pure state. M.p. 170°. This value concerns a partially resolved sample. (Found: C, 65·49; H, 8·73; Br, 25·77. $C_{18}H_{29}Br$ requires: C, 66·45; H, 9·98; Br, 24·5%). The mass spectrum shows a doublet of equal intensity at *m/e* 326–324 and a singlet at 245 (most intense peak).

2-Perhydrotriphenylenylcarbinol (XVIII) was obtained by LAH reduction of methyl ester of XV in ether. It was recrystallized from MeOH, yield 90%, m.p. 173°; mass spectrum: *m/e* 276 (M), 258 (M-18), 245, 189.

Dodecahydrotriphenylen-2-carboxylic acid (XX). Compound XIX (4·3 g),[17] dissolved in heptane (100 ml), was hydrogenated in the presence of Pd/C at 10% (0·5 g) at 200° for 48 hr, under 100 atm of H_2. After cooling, 3 g of XX precipitated, m.p. 260° (from EtOH or benzene), yield 70%. (Found: C, 80·36; H, 8·80 equiv wt 284. $C_{19}H_{24}O_2$ requires: C, 80·24; H, 8·51%, equiv wt 284). Ethyl ester of XX: m.p. 90°. (Found: C, 80·81; H, 9·09. $C_{21}H_{28}O_2$ requires: C, 80·73; H, 9·03%).

Dodecahydrotriphenylen-1-one (XXI). CrO_3 (10 g) dissolved in hot AcOH (250 ml) was added dropwise to XI (10 g) suspended in AcOH (50 ml). The mixture was heated on a steam bath for 5 hr. The undissolved fraction was filtered off hot (4 g of unreacted XI) and the filtrate diluted with water. 4·2 g of XXI were obtained, m.p. 224° (from 3:1 EtOH–water), 60% conversion, yield 65%. (Found: C, 83·71; H, 8·60. Calc. for $C_{18}H_{22}O$: C, 84·99; H, 8·72%), oxime m.p. 198°; 2,4-dinitriphenylhydrazone, m.p. 267°. (Found: C, 65·96; H, 6·34; N, 12·88. Calc. for $C_{24}H_{26}O_4N_4$; C, 66·34; H, 6·03; N, 12·90%).

Dodecahydrotriphenylen-1-ol (XXII). XXI (5 g) dissolved in anhyd THF (100 ml) was added dropwise to a boiling suspension of LAH (0·52 g) in THF (20 ml), refluxed for 3 hr and worked-up as before. The product was recrystallized from acetone (3·5 g), yield 70%, m.p. 160°. (Found: C, 82·06; H, 9·36. $C_{18}H_{24}O$ requires: C, 84·32; H, 9·44%).

2-Methoxydodecahydrotriphenylene (XXIV). XXIII (3 g),[18] dissolved in heptane (100 ml), was hydrogenated in the presence of Pd/C at 10% (0·3 g). The temp was maintained at 150° for 5 hr, under 50 atm H_2, 1·7 g of XXIV was obtained, m.p. 75–77° (from heptane or EtOH). (Found: C, 84·28; H, 9·88. $C_{19}H_{26}O$ requires: C, 84·39; H, 9·69%).

Acknowledgements—The authors are deeply indebted to Dr. Anna Laura Segre for running the NMR spectra and to Dr. Antonio Selva for measuring the mass spectra and to Drs. Gianluigi Triveri and Roberto Capellini for their valid experimental contribution.

REFERENCES

1 M. Farina, *Tetrahedron Letters* 2097 (1963).
2 M. Farina, G. Allegra and G. Natta, *J. Am. Chem. Soc.* **86**, 516 (1964).
3 W. Schrauth and K. Görig, *Ber. Dtsch. Chem. Ges.* **56**, 2024 (1923).
4 M. Farina and G. Audisio, *Tetrahedron Letters* 1285 (1967).
5 M. Farina, G. Audisio and P. Bergomi Bianchi, *Chimica e Industria Milan* **50**, 446 (1968).
6 G. Allegra, M. Farina, A. Immirzi, A. Colombo, U. Rossi, R. Broggi and G. Natta, *J. Chem. Soc.* B, 1020 (1967).
7 G. Allegra, M. Farina, A. Colombo, G. Casagrande Tettamanti, U. Rossi and G. Natta, *Ibid.* B, 1028 (1967).
8 C. Mannich, *Ber. Dtsch. Chem. Ges.* **40**, 153 (1907).
9 C. M. Buess and D. D. Lawson, *Chem. Rev.* **60**, 313 (1960).
10 W. Reppe, *Liebigs Ann.* **596**, 135 (1955).
11 D. Häusigk and G. Kölling, *Chem. Ber.* **101**, 469 (1968).
12 A. L. Segre and J. I. Musher, *J. Am. Chem. Soc.* **89**, 706 (1967).
13 G. Allegra, M. Farina, A. Immirzi and R. Broggi, *Tetrahedron Letters* 1975 (1964).
14 M. Farina, G. Allegra, F. Logiudice and U. Pedretti, *Ibid.* 551 (1969).

[15] M. S. Kharash and H. C. Brown, *J. Am. Chem. Soc.* **64**, 329 (1942).
[16] F. Runge, *Zeitschrift für Elektrochemie* **60**, 957 (1956).
[17] C. C. Barker, R. G. Emmerson and J. D. Periam, *J. Chem. Soc.* 4482 (1955).
[18] W. S. Rapson, *Ibid.* 15 (1941).