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SYNTHESIS AND PROTON MAGNETIC RESONANCE STUDIES OF SOME 1,2-DIALKYL-1,2-BIS(2,6-DIMETHYLPHENYL)ETHANES

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Abstract—Compounds of the type $R_1R_2CH—CHR_2R_1$, in which R_1 is 2,6-dimethylphenyl and R_2 is hydrogen, methyl, or t-butyl, were synthesized and the *meso* and *racemic* isomers separated. A study of these compounds by PMR spectroscopy, including ^{13}C-satellites and the effects of temperature variation, yielded information about the configurations, the preferential conformations, and the barriers to rotations about the R_1—CH bonds.

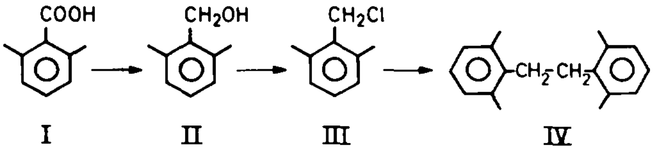
INTRODUCTION

OUR investigations of sterically hindered derivatives of neopentylbenzene[1] included the synthesis of 2,6-dimethylneopentylbenzene (Scheme **2**). The ultimate step in this synthesis—the reduction of 2,6-dimethyl-(2,2-dimethyl-1-chloropropyl)benzene (XIII) with lithium in liquid ammonia—gave the desired product in 87% yield, together with small amounts of the two stereoisomers of 3,4-bis(2,6-dimethylphenyl)-2,2,5,5-tetramethylhexane (XV). PMR spectra of the compounds were obtained and interpreted assuming preferential conformations arrived at by a study of molecular models. It was concluded that the isomer with m.p. 216·0–218·0° is *meso*, and that with m.p. 224·5–226·0° is (±)-3,4-bis(2,6-dimethylphenyl)2,2,5,5-tetramethylhexane. In addition to this result the spectra revealed that considerable hindrance to rotation about the aryl-CH bonds is present in both compounds. This phenomenon, and the wish to support the assumptions made with factual data, led us to the synthesis and an extensive PMR investigation of the related compounds, 1,2-bis(2,6-dimethylphenyl)ethane (IV), *meso*- and (±)-2,3-bis(2,6-dimethylphenyl)butane (X).

CHEMISTRY

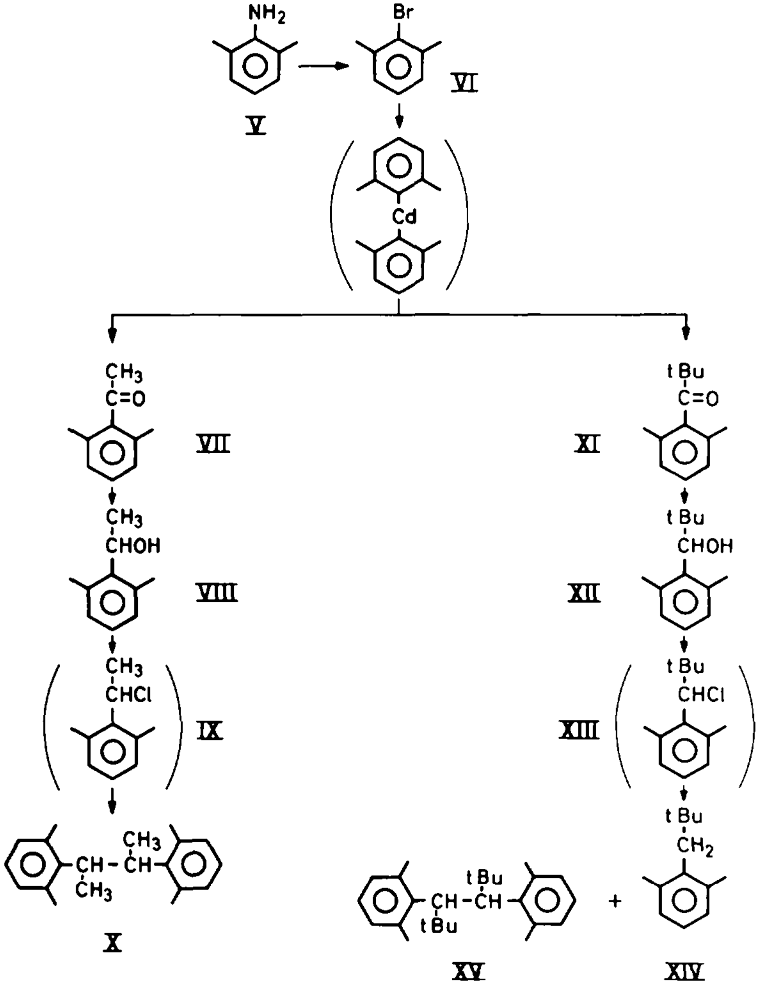
1,2-Bis(2,6-dimethylphenyl)ethane (IV) was obtained by a sequence of reactions (Scheme **1**), starting from 2,6-dimethylbenzoic acid (I).

SCHEME 1



The other four compounds, *meso*- and (±)-2,3-bis(2,6-dimethylphenyl)butane (X), and *meso*- and (±)-3,4-bis(2,6-dimethylphenyl)-2,2,5,5-tetramethylhexane (XV), were synthesized from 2,6-dimethylaniline (V) (Scheme **2**).

SCHEME 2



In connection with these syntheses the following remarks should be made. (i) The yield of ketones VII and XI from the reaction between the organocadmium compound and the acid chlorides can be raised considerably if about 60% of the ether, in which the organocadmium compound has been formed, is removed, and replaced by benzene *prior* to the addition of the acid halide. It was found inconvenient and unnecessary to remove all of the ether, as Cason[2] recommends. (ii) The use of tetrahydrofuran throughout the reactions from VI to XI leads to the formation of substantial amounts of 4-bromobutyl pivalate, $BrH_2C—CH_2—CH_2—CH_2\,OCOC(CH_3)_3$. We have found similar products from the reactions of Grignard reagents with acid halides in tetrahydrofuran, showing the instability of the solvent under these conditions. (iii) The method of Kharasch and Sayles[3] was used for the dimerization of the chlorides III and IX. *meso*-X and *meso*-XV were isolated by crystallization, (±)-X was obtained by preparative GLC and (±)-XV was purified by repeated recrystallization.

PMR spectra

PMR spectra (60 MHz) were obtained from the compounds as solutes in different solvents and at various temperatures. Chemical shifts and coupling constants for solutions in carbon tetrachloride at ordinary probe temperature are collected in the Table. ^{13}C-satellites of the proton signals were obtained by time averaging over several hundreds to several thousands of scans, depending on the solubility of the compound.

The aromatic Me groups of compound IV give one singlet, as do the methylene protons. The ^{13}C-satellites of the methylene proton signal[4,5] form the AA'-part of an AA'BB'X-system, in which A and A' are the magnetically nonequivalent protons of a $^{13}CH_2$-group, B and B' those of the $^{12}CH_2$-group in the same molecule and X is the ^{13}C-nucleus. To obtain the vicinal proton–proton coupling constants, J_{AB} and $J_{AB'}$, the AA'-part was analysed according to general methods for AA'BB'-systems,[6,7] with the assumption that J_{BX} and $J_{B'X}$, corresponding to coupling between the ^{13}C-nucleus and the protons of the $^{12}CH_2$-group, can be taken to be zero.[8] We had to rely on "reasonableness" as a criterion in the calculations, because the use of spin-tickling techniques[9] was out of question under the circumstances.

The aromatic Me groups of *meso*-X, (±)-X, *meso*-XV and (±)-XV give two singlets. The separation between the signals is largest for (±)-X and (±)-XV. The protons of the methyl and methine groups of the butane moiety of *meso*-X and (±)-X form $AA'X_3X'_3$-systems. These were analysed[10,11] to yield the important coupling constants, $J_{AA'}$. The protons of the t-Bu groups and those of the methine groups of *meso*-XV and (±)-XV give singlets. The ^{13}C-satellites of the methine proton signals are A-parts of ABX-systems, in which A is the proton of a $^{13}CHR_2$-group, B the proton of the $^{12}CHR_2$-group in the same molecule, and X the ^{13}C-nucleus; again $J_{BX} = 0$.

The signals of the aromatic protons of compounds (±)-X and (±)-XV form ABC-patterns, indicated in the Table by (m). Those of *meso*-X and *meso*-XV appear as singlets.

The spectrum of compound IV (in methylene chloride) did not change on cooling the sample to −60°. On raising the temperature of samples of *meso*-X and (±)-X (in chlorobenzene), it was found that the aromatic Me signals broaden gradually, and coalesce at 104° and 171° respectively. The $AA'X_3X'_3$-systems did not change visibly. The ABC-pattern of the aromatic protons of (±)-X becomes a singlet at high temperatures. The spectra of *meso*-XV and (±)-XV underwent no change up to 200°.

DISCUSSION

In a discussion of the PMR data of our compounds we have to consider the possible conformations of the ethane system and of the aryl groups with respect to the ethane part of the molecule. Two possibilities for each conformational system can be distinguished: (i) only one conformation is present, and (ii) an equilibrium exists between different conformations. For ethane systems in general only the three staggered conformations are taken into account in the case of an equilibrium,[12] although some interesting results have been obtained by assuming a thermal distribution over all angles of rotation.[13] No general treatment seems to exist for systems in which an aryl group is bonded to a tetravalent C atom.[14] Here it is sufficient to note that the two Me groups of a 2,6-dimethylphenyl group attached to a tetravalent C atom,

TABLE. PMR DATA OF COMPOUNDS $R_1R_2CH—CHR_2R_1$[a] IN CCl_4 AT 39°

Compound	R_2	m.p. °C	Chemical Shifts (δ-values, ppm, from TMS)				Coupling Constants (Hz)		
			Arom. CH_3	R_2	$R_1R_2C\underline{H}$	Arom. H	$R_1R_2{}^{13}\underline{C}—\underline{H}$	$R_1R_2C\underline{H}—C\underline{H}R_2R_1$	$R_1\underline{R_2}—C\underline{H}$
IV	H	122·5–123·5	2·23	2·80	2·80	6·92 (s)	126	10[b] 6[b]	14[c]
meso-X	CH_3	140·0–141·5	2·42 2·56	1·05	3·90	6·88 (s)	—	12	7·4
(±)-X	CH_3	53·0 54·0	1·67 2·47	1·45	3·68	6·73 (m)	—	9·5	7·7
meso-XV	$C(CH_3)_3$	216·0–218·0	2·55 2·68	0·72	4·23	6·95 (s)	126	12[b]	0·5[d]
(±)-XV	$C(CH_3)_3$	224·5–226·0	1·47 2·53	1·12	4·10	6·70 (m)	126	5[b]	0·5[d]

[a] R_1 = 2,6-dimethylphenyl

[b] Obtained from ^{13}C-satellites; values given are ±0·5 Hz.

[c] Values in the range of 14 ± 2 Hz are compatible with the ^{13}C-satellite bands.

[d] Estimated from line-widths.

(s) singlet

(m) multiplet; values given are for "centres of gravity".

bearing three different ligands (Fig. 1, $R_1 \neq R_2 \neq R_3 \neq R_1$, $X_1 = X_2 = CH_3$), can only become chemically equivalent if rotation about the bond by 180° is allowed.[15] The PMR spectra can be temperature-dependent due to changes in population or rates of interconversion of conformers.[16]

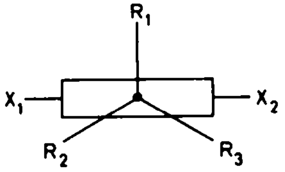


FIG. 1

(a) 1,2-*Bis*(*2,6-dimethylphenyl*)*ethane* (IV). The observed singlet for the four aromatic Me groups, and also that for the four methylene protons, show that the four Me groups (and the methylene protons) are chemically equivalent, either because the molecule exists in one conformation with proper symmetry or there is a fast equilibrium between conformers. In the former case the aryl groups must be in *trans* position and the planes of the benzene rings must be perpendicular to the plane through the ethane and aryl-CH_2 bonds. In the case of fast interconversion of conformers, chemical equivalence of the aromatic Me groups can be reached by rotation about the aryl-CH_2 bonds, by rotation about the ethane bond, or about both types of bonds simultaneously. The observed pattern for the ^{13}C-satellites cannot be used to distinguish between the two cases. The actual value for the vicinal coupling constants J_{AB} and $J_{AB'}$ can be explained by assuming that torsional vibrations about the pure *trans* orientation are allowed, or that a fast equilibrium exists between unequal populations of the *trans* and *gauche* conformations of the ethane moiety.[17] In the latter case using the values of 12 Hz for coupling between protons in *trans* position (J_t), and 5 Hz for the *gauche* position (J_g),* it is calculated that the equilibrium is between ~70% of the *trans* conformation and ~15% of each of the *gauche* conformations.

The PMR data do not allow a conclusion regarding the preferential conformations of the 2,6-dimethylphenyl groups with respect to the methylene groups, nor can they yield an estimation of the barriers to rotation of the aryl groups. However, it was found for bibenzyl[18] that the benzene rings are preferentially perpendicular to the plane through the aryl-CH_2 and ethane bonds, due to steric interaction of the *ortho* protons with the methylene protons. Substitution of these protons by Me groups should lead to an increase of the sterical factor. Therefore we conclude that in the preferential conformation of IV the aryl groups are in *trans* position to each other with the planes of the aryl groups perpendicular to the plane through the aryl-CH_2 and ethane bonds.

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* Several "standard" values for these constants are found in the literature: $J_t = 10{\cdot}2$–$16{\cdot}5$ Hz, $J_g = 2{\cdot}0$–$2{\cdot}6$ Hz;[16] $J_t = 9$–18 Hz, $J_g = 1{\cdot}2$–$3{\cdot}5$ Hz;[5] $J_t = 11$ Hz, $J_g = 5$ Hz;[12a] $J_t = 10$–12 Hz, $J_g = 1$–3 Hz;[11] $J_t = 13$ Hz, $J_g = 3$ Hz;[10] we consider compounds *meso*-XV and (±)-XV as good models for J_t and J_g in 1,2-diarylethanes, see part c. of this discussion.

(b) meso- *and* (±)-*2,3-Bis(2,6-dimethylphenyl)butane* (X). The fact that the four aromatic Me groups give two singlets at ordinary temperature can only be explained by slow rotation about the aryl-CHR_2 bonds (on the PMR time-scale).

The other possibility could have been, that the two aryl groups are nonequivalent. If rotation about the aryl-CHR_2 bonds were fast, the two Me groups of one aryl group would give one singlet. Nonequivalency of the aryl groups could occur if rotation about the ethane bond were slow, but then only for the *meso* compound. In the *racemic* isomer the aryl groups are equivalent in any conformation because of a two-fold axis of symmetry (Fig. 3). In the *meso* compound there is no such axis in conformations **b** and **c** (Fig. 2). Consequently, in those conformations the Me groups (R_2 and R'_2) and the methine protons (H and H') of the butane system are chemically nonequivalent. However, this is not consistent with the observed $AA'X_3X'_3$-pattern for this part of the molecule. The compound exists either in conformation **a**, or there is a fast equilibrium between all three conformations **a**, **b** and **c**. The same conclusion derives from the observed ABC-pattern for the aromatic protons as compared with the expected overlapping A_2B-pattern of two nonequivalent, fast rotating aryl groups.

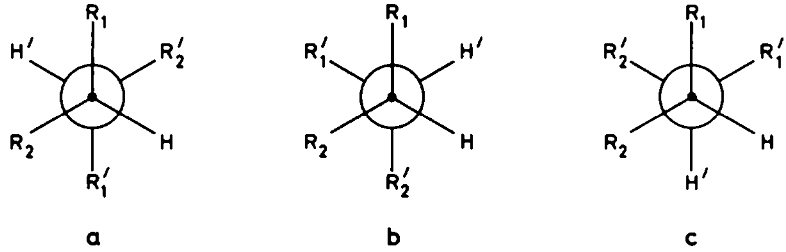

Fig. 2. *meso*-1,2-Di-R_2-1,2-bis(2,6-dimethylphenyl)ethane

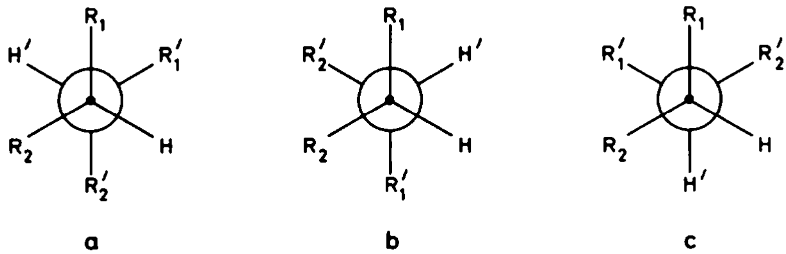

Fig. 3. (±)-1,2-Di-R_2-1,2-bis(2,6-dimethylphenyl)ethane

The difference in chemical shifts of the two Me groups of one and the same aromatic ring is due to the chirality of the group CHR_2—CHR_2Ar in both compounds. This "asymmetry effect",[20] Δ, is different for the two isomers: 0·14 ppm for the compound with m.p. 140·0–141·5°, and 0·80 ppm for that with m.p. 53·0–54·0°. A large contribution to this effect is expected of a conformation in which the aryl groups are in *gauche* position, as in conformations **b** and **c** (Fig. 2) for the *meso* isomer, or in **a** and **b** (Fig. 3) for the *racemic* isomer. In such a conformation one of the Me groups of each ring lies in the shielding region of the other ring, while the other Me group is in the deshielding region.[21] However, if both *gauche* conformations contribute and interconversion is fast, the result would be an upfield shift for both Me signals and, consequently, a smaller "asymmetry effect", because both Me groups spend part of their time in the shielding region of the other ring.

A decision about the configurations and conformations of the two compounds can be made if the vicinal coupling constants of the methine protons are also taken into account. For the isomer with m.p. 140·0–141·5° the observed vicinal coupling constant of 12 Hz and the smaller value for the "asymmetry effect" corresponds to the conformation **a** of the *meso* compound (Fig. 2). This is also the only conformation present, because it was found that the spectrum does not change between 40 and 200°. For the other isomer, with m.p. 53·0–54·0°, the larger "asymmetry effect" is in conformity with conformations **a** and **c** of the *racemic* compound. The observed vicinal coupling constant of 9·5 Hz does not correspond with either of these two conformations. It is possible that a mixture of the two conformations is in a fast equilibrium or that the conformation resembles conformation **a** but with a dihedral angle between the two protons differing from 180°. For the former case it is calculated that ~65% is in conformation **a** and ~35% in conformation **b** and **c**. The dihedral angle, corresponding to a vicinal coupling constant of 9·5 Hz, calculated by means of the Karplus-equation,[19] taking $J_{180^\circ} = 12$ Hz and $\kappa = 0$, is 150°. The fact that the spectrum does not change between 40 and 200°, and the near constancy of the chemical shift of one aromatic Me signal (Table) are in favour of the conclusion that the *racemic* isomer exists in one conformation. This result is the same as that obtained by Bonn and Weill[21] for the two isomers of 2,3-diphenylbutane.

The barriers to rotation about the aryl-CHR$_2$ bonds, as calculated from the differences in chemical shift of the two aromatic Me signals at ordinary temperature and the coalescence temperatures,[22] are $\Delta G^\ddagger_{104^\circ} = 24$ kcalmole^{-1} for the *meso* compound and $\Delta G^\ddagger_{171^\circ} = 19$ kcalmole^{-1} for the *racemic* compound. It is possible that the higher value obtained for the *meso* compound is caused by interaction of the Me group of one CHR$_2$-part of the molecule with the aromatic Me groups of the aryl group on the other (R$_2$ with R$'_1$, and R$'_2$ with R$_1$, Fig. 2, **a**), as indicated by a study of molecular models. This phenomenon is under investigation at the moment.

Our conclusions, apart from those about the configurations of the compounds, are, that both isomers are in a fixed conformation, *meso* in one in which the substituents of the ethane system are pair-wise in *trans* position, while in the *racemic* isomer the substituents are pair-wise in *gauche* position, with a distortion of 30° from the "ideal" conformation **a** (Fig. 3). Molecular models indicate that the dihedral angle between the two Me groups has become smaller than 60° as in conformation **a**, or in other words, the 2,6-dimethylphenyl groups are more space-demanding than the Me groups.

(c) meso- *and* (±)-3,4-*Bis*(2,6-*dimethylphenyl*)2,2,5,5-*tetramethylhexane* (XV). From general steric considerations, and also from inspection of models it is expected that the t-Bu groups tend to be in *trans* position in both isomers. For the *meso* compound this is the case in conformation **a** (Fig. 2, with R$_2$ = R$'_2$ = t-Bu), in which all other groups are pair-wise in *trans* position. As for *meso*-2,3-bis(2,6-dimethylphenyl)butane this arrangement should lead to a low value of the "asymmetry effect" in the signals of the aromatic Me groups, and a vicinal coupling constant of the methine protons close to 12 Hz. This is observed (cf. Table) for the compound with m.p. 216·0–218·0°.

For the *racemic* isomer conformation c (Fig. 3, $R_2 = R'_2$ = t-Bu) is that in which the two t-Bu groups are in *trans* position. The aromatic groups are in *gauche* position to each other; consequently, a large "asymmetry effect" in the signals of the aromatic Me groups is expected. Furthermore, the two methine protons are in *gauche* position for which a value of the vicinal coupling constant of about 5 Hz is expected. This is indeed found for the isomer with m.p. 224·5–226·0°. A perspective drawing of the preferential conformation of the *racemic* isomer is given in Fig. 4. From this the position of one of the two Me groups of each aromatic ring in the shielding region of the other ring is evident. A slight deviation from 180° for the dihedral angle between the two C-t-Bu bonds has been introduced in accordance with Courtauld-models of the compound.

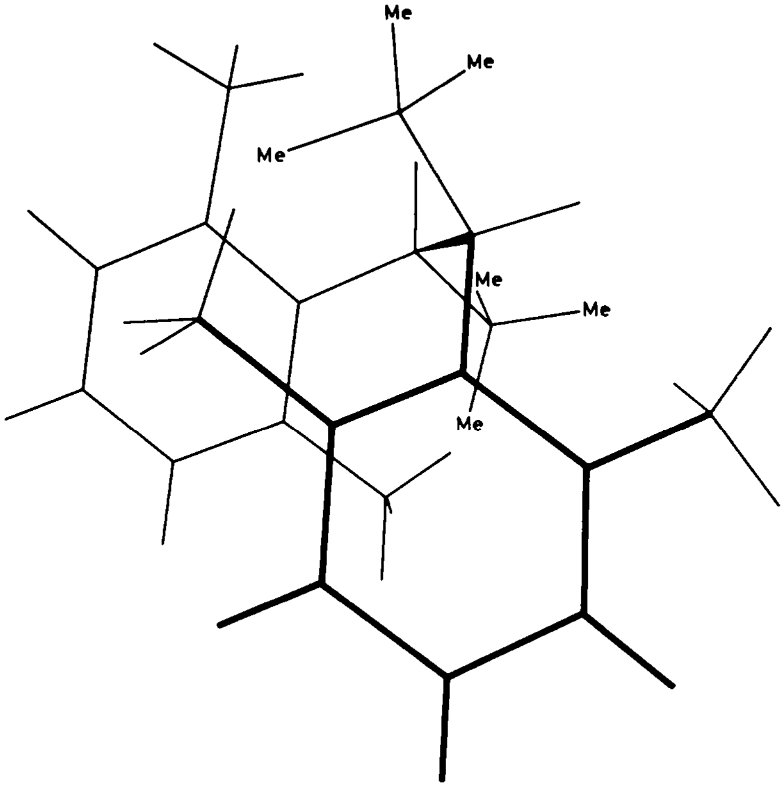

Fig. 4

Rotation about the aryl-CHR_2 bonds is completely inhibited in both isomers as shown by the absence of change in the spectra upon raising the temperature up to 200°. This observation compares with the recently established fact that 3-pivaloyl-2,4,6-trimethylbenzoic acid can be separated into optical antipodes because of inhibition of rotation about the aryl-pivaloyl bond.[23]

EXPERIMENTAL

The elemental analyses were performed by Mr. M. van Leeuwen of this Laboratory. All m.ps and b.ps are uncorrected. 60 MHz PMR-spectra were obtained on a Varian A-60 spectrometer; a C-1024 Time Averaging Computer was used for the ^{13}C-satellites.

1,2-*Bis(2,6-dimethylphenyl)ethane* (IV)

2,6-*Dimethylbenzyl alcohol* (II) was obtained in 90% yield from I by reduction with LAH in anhyd ether; b.p. 138–140°/20 mm (lit.[24] b.p. 118–120°/13 mm).

2,6-*Dimethylbenzyl chloride* (III). Treatment of II with $SOCl_2$ in dry benzene gave III in 62% yield, b.p. 98–100°/15 mm (lit.[25] 96–97°/13 mm).

1,2-*Bis(2,6-dimethylphenyl)ethane* (IV). 10·4 g (0·067 mole) of III was dimerized according to the method of Kharasch and Sayles[3] which gave 5·2 g (65%) of crude IV. Recrystallization from MeOH and sublimation gave pure IV, m.p. 123·5–124·5° (lit.[26] m.p. 124–125°).

2,3-*Bis(2,6-dimethylphenyl)butane* (X)

2,6-*Dimethylbromobenzene* (VI) was obtained in 42% yield from V by diazotation in 40% HBr and treatment with freshly prepared Cu powder, b.p. 84–85°/16 mm, n_D^{25} 1·5495 (lit.[27] b.p. 98–99°/20 mm, n_D^{20} 1·5552).

2,6-*Dimethylacetophenone* (VII). In a 1 l. 5-necked flask equipped with a mechanical stirrer, a thermometer, a gas inlet tube, a dropping funnel and a reflux condenser was placed 22·1 g (0·91 mole) Mg turnings and 90 ml anhyd ether. 168·0 g (0·91 mole) of VI was dissolved in 360 ml ether. In an atmosphere of dry N_2 25 ml of this solution together with 1 ml 1,2-dibromoethane was added to the Mg. The flask was heated until the reaction started, and the rest of the soln was added dropwise. After the addition was completed the reaction mixture was stirred for 30 min at room temp. The flask was then cooled in ice-water and while the mixture was stirred rapidly 90·0 g (0·49 mole) anhyd $CdCl_2$ was introduced. The reaction mixture was stirred for 1 hr. Part of the ether was distilled off (60%) and replaced by dry benzene. While the mixture was heated under reflux 70·0 g (0·89 mole) of freshly distilled acetyl chloride was added dropwise. After the addition was complete the reaction mixture was refluxed for another 1·5 hr. It was then hydrolysed with 4N H_2SO_4 and worked up in the usual way yielding 82·0 g (62%) of VII, b.p. 107–108°/18 mm, n_D^{20} 1·5138 (lit.[28] 110–112°/23 mm, n_D^{22} 1·5160).

1-(2,6-*Dimethylphenyl)ethan*-1-*ol* (VIII). VII was reduced with LAH in ether to yield 84% crude VIII. A sample was recrystallized twice from pentane, m.p. 68·0–69·0° (lit.[29] m.p. 68·5–69·5°).

1-(2,6-*Dimethylphenyl*)1-*chloroethane* (IX). In a 500 ml 4-necked flask equipped with a mechanical stirrer, a thermometer, a dropping funnel, and a reflux condenser was placed 46·0 g (0·306 mole) of VIII, 37·1 g (0·306 mole) purified[30] N,N-dimethylaniline and 200 ml dry benzene. A soln of 55·0 g (0·462 mole) purified $SOCl_2$ in 100 ml dry benzene was added slowly. The temp of the reaction mixture was kept between 0 and 5° by means of an ice-bath. After all the $SOCl_2$ had been added the temp was allowed to raise to 20° and the reaction mixture was kept at this temp for 4 hr. The two resulting layers were separated and the upper layer washed 4 times with ice-water. After drying over $MgSO_4$ the solvent and the excess $SOCl_2$ were evaporated off *in vacuo*; 100 ml dry benzene was added and evaporated off; this procedure was repeated again. The resulting syrupy liquid was used without further purification in the next step.

2,3-*Bis(2,6-dimethylphenyl)butane* (X). In a 1 l. 5-necked flask equipped with a mechanical stirrer, two gas inlet tubes, a thermometer, and a reflux condenser a soln of MeMgBr was prepared in an atmosphere of dry N_2 from 28·4 g (1·17 moles) Mg turnings, 100·0 g (1·05 moles) gaseous MeBr and 500 ml anhyd ether. The resulting soln was freed from unreacted Mg by filtration, 27·3 g (0·21 mole) anhyd cobaltous chloride was added. After 30 min stirring a soln of IX in 100 ml anhyd ether was introduced slowly. The resulting mixture was refluxed for 3 hr. The reaction mixture was then cooled in an ice-salt bath and 300 ml 10% AcOH was added. After 1 hr the black ppt was filtered off and washed 3 times with ether. The combined ethereal layers were washed with water and dried over $MgSO_4$. The ether was evaporated off and the residue was freed from volatile compounds by distillation *in vacuo* (up to 100°/9 mm flask temp). The distillation residue was taken up in boiling pet. ether (b.p. 60–80°). After cooling to room temp the crystals were filtered off and sublimed at 130° and 0·1 mm, yielding 5·5 g *meso*-X, m.p. 140·0–141·5°. The mother liquor was distilled *in vacuo* and the fraction boiling from 120 to 160°/1·5 mm was collected. The oil obtained was diluted with 25 ml pet. ether and cooled to −30°. The crystals were filtered off and recrystallized from acetone to give another 1·2 g *meso*-X, m.p. 140·0–141·2°. The two fractions were combined and sublimed to yield 6·6 g (16·2%) *meso*-2,3-bis(2,6-dimethylphenyl)butane, m.p. 140·0–141·5°. (Found: C, 90·3; H, 9·9. Calc. for $C_{20}H_{26}$: C, 90·16; H, 9·84%).

The mother liquors were combined, freed from solvents and subjected to preparative gas chromatography (2 m Apiezon L column at 210°). Distillation of the fraction collected (b.p. 142°/1·5 mm) yielded an oil, which solidified upon standing. The crystals were taken up in a two-fold volume of dry MeOH, warmed to 60°, and cooled to room temp. The soln was seeded and cooled further to 0°. The white crystals formed were filtered off to give 4·1 g of (±)-X, m.p. 53·0–54·0°. The filtrate was heated to 60° and part of the MeOH was evaporated. The soln was cooled to room temp, seeded, and cooled further to 0°. In this way another 0·9 g of (±)-X was obtained. A total 5·0 g (12·3%) of (±)-2,3-bis(2,6-dimethylphenyl)butane was obtained altogether. (Found: C, 90·3; H, 9·7. Calc. for $C_{20}H_{26}$: C, 90·16; H, 9·84%).

3,4-*Bis*(2,6-*dimethylphenyl*)2,2,5,5-*tetramethylhexane* (XV)

2,6-*Dimethylpivalophenone* (XI). To a soln of 1·0 mole of 2,6-dimethylphenylmagnesium bromide in 500 ml anhydrous ether was added 96·0 g (0·52 mole) anhydrous $CdCl_2$. The resulting mixture was heated under reflux for 1 hr and subsequently part of the ether was distilled off (60%) and replaced by dry benzene. At reflux temp 98·0 g (0·81 mole) pivaloyl chloride (prepared according to Brown,[31] b.p. 105–106°) was introduced slowly. The reaction mixture was stirred vigorously and refluxed for another 1·5 hr. It was then worked up in the usual way to yield 95·0 g (50%) of XI, b.p. 128–130°/18 mm. A sample was redistilled b.p. 126°/16 mm, n_D^{25} 1·5013, and analysed. (Found: C, 82·0; H, 9·7. Calc. for $C_{13}H_{18}O$: C, 82·06; H, 9·53%).

The same reaction was carried out once in THF in order to avoid the replacement of solvent during the course of the reaction. There was obtained a mixture of XI and a compound, which was identified by elemental analysis (Found: Br, 32·8. Calc. for $C_9H_{17}BrO_2$: Br, 33·70%) and PMR spectroscopy as 4-bromobutyl pivalate. Separation of XI and this compound was effected by preparative gas chromatography.

1-(2,6-*Dimethylphenyl*)2,2-*dimethylpropan*-1-*ol* (XII). 100·0 g (0·53 mole) of XI was reduced with LAH in anhyd ether, yielding 99·0 g (98%) of crude XII, m.p. 71–74°. Recrystallization from MeOH–water (2:1) raised the m.p. to 74·9–75·3°. (Found: C, 81·3; H, 10·5. Calc. for $C_{13}H_{20}O$: C, 81·20; H, 10·48%).

1-(2,6-*Dimethylphenyl*)2,2-*dimethyl*-1-*chloropropane* (XIII). 100·0 g (0·52 mole) of XII was treated with 152·7 g (1·28 moles) $SOCl_2$ in 500 ml dry benzene. The product obtained after evaporation of the solvent and the excess $SOCl_2$ was used as such in the next step.

3,4-*Bis*(2,6-*dimethylphenyl*)2,2,5,5-*tetramethylhexane* (XV) and 2,6-*dimethylneopentylbenzene* (XIV). The crude XIII was dissolved in 400 ml dry pentane and added to a soln of 12·0 g (1·73 moles) Li in 1000 ml liquid ammonia. After 8 hr the reaction mixture was treated with 500 ml water. The aqueous layer was separated and extracted with two 200-ml portions pentane. The combined pentane layers were washed with 2N HCl and water. After drying over $MgSO_4$ the pentane was evaporated, and the residue distilled *in vacuo* to yield 80·0 g (87%) of XIV, b.p. 106–109°/15 mm.

The distillation residue, which solidified partly at room temp was taken up in boiling acetone–benzene (1:1). The crystals deposited at room temp were filtered off and recrystallized five times from acetone–benzene. Sublimation at 150° and 0·1 mm yielded 0·4 g (0·4%) *meso*-3,4-bis(2,6-dimethylphenyl)-2,2,5,5-tetramethylhexane, m.p. 216·0–218·0°. (Found: C, 89·2; H, 10·9. Calc. for $C_{26}H_{38}$: C, 89·07; H, 10·93%).

The mother liquors were combined and evaporated to dryness. The residue was extracted several times with boiling hexane. All the hexane extracts were evaporated to dryness and the resulting crystals were recrystallized first from EtOH and then eight times from acetone. There was obtained 0·3 g (0·3%) of (±)-3,4-bis(2,6-dimethylphenyl)2,2,5,5-tetramethylhexane, m.p. 224·5–226·0°. (Found: C, 89·0; H, 10·9 Calc. for $C_{22}H_{38}$: C, 89·07; H, 10·93%).

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