1,1′-SPIROBIINDANES[1]

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Received June 24, 1963

ABSTRACT

The product from both the acid-catalyzed cyclodehydration of 4-methyl-4-phenyl-2-pentanone (I*a*) described by Hoffman (1) and by Barnes and co-worker (2) and the reaction of the saturated cyclic dimer of α-methylstyrene with aluminum chloride reported by Adams and co-workers (3) was shown to be 3,3,3′,3′-tetramethyl-1,1′-spirobiindane (IX*a*) by Curtis (4). A mechanism is postulated to explain the formation of the 1,1′-spirobiindane system. The reactions of several polyalkylindenes with α-methylstyrene and triphenylcarbinol were investigated. Several new polyalkyl-1,1′-spirobiindanes and a new polyalkylindene[1,2-*a*]indene were produced. Two of the 1,1′-spirobiindanes investigated were synthesized by unequivocal methods.

In 1929 Hoffman (1) reported the formation of a hydrocarbon from the treatment of 4-methyl-4-phenyl-2-pentanone (I*a*) with anhydrous zinc chloride at 180°. Later Barnes and co-worker (2) observed the formation of a hydrocarbon in low yield from refluxing 4-methyl-4-(*p*-tolyl)-2-pentanone (I*b*) with 50% sulphuric acid. Relating their work to that of Hoffman, they proposed after a thorough study that the compound he obtained was 4*b*,9,9,10,10-pentamethyl-4*b*,9,9*a*,10-tetrahydroindeno[1,2-]indene (VI*a*) and postulated the mechanism illustrated in Chart I to explain its formation.

Barnes and co-worker proposed that the beta-aryl ketone (I*a*) can undergo two simultaneous reactions. It can eliminate acetone by acid cleavage to yield the protonated α-methylstyrene (II*a*) and it can undergo cyclodehydration to yield the 1,1,3-trimethylindene (IV*a*). The carbonium ion II*a* then attacks the indene (IV*a*) at carbon 2 so as to produce the new carbonium ion (V), which alkylates the adjacent benzene ring to produce VI*a*.

In 1959 Adams and co-workers (3) reported the formation of (VI*a*) by the treatment of the saturated cyclic dimer of α-methylstyrene (1-phenyl-1,3,3-trimethylindane) with aluminum chloride at 180°. The mechanism proposed involved the formation of protonated α-methylstyrene (II*a*) and indene (IV*a*) from the indane by acid cleavage. These were postulated to react as illustrated in Chart I.

More recently Curtis (4) demonstrated by nuclear magnetic resonance (n.m.r.) studies that the product obtained by all these workers was not the polyalkylindeno[1,2-*a*]indene (VI*a*) but really the 3,3,3′,3′-tetramethyl-1,1′-spirobiindane (IX*a*). He later substantiated this (5) by carrying out a number of interconversions of the 1,1′-spirobiindanes.

In the light of this evidence, the mechanisms of the above reactions became of interest since those postulated by Barnes and Adams could not account for the formation of IX*a*. However, it is interesting to note that in the mechanisms proposed by these workers, two reactants, the indene (IV*a*) and the carbonium ion (II*a*), are present. The following new mechanism for the formation of (IX*a*), illustrated in Chart II, is proposed.* An equilibrium can be set up in the acid medium between the endocyclic form of the 1,1,3-trimethylindene (IV*a*) and the exocyclic form (VII*a*) ($R_1 = R_2 = H$). (The 1,1,3-trimethylindene could form as illustrated in Chart I or could be added as one of the starting

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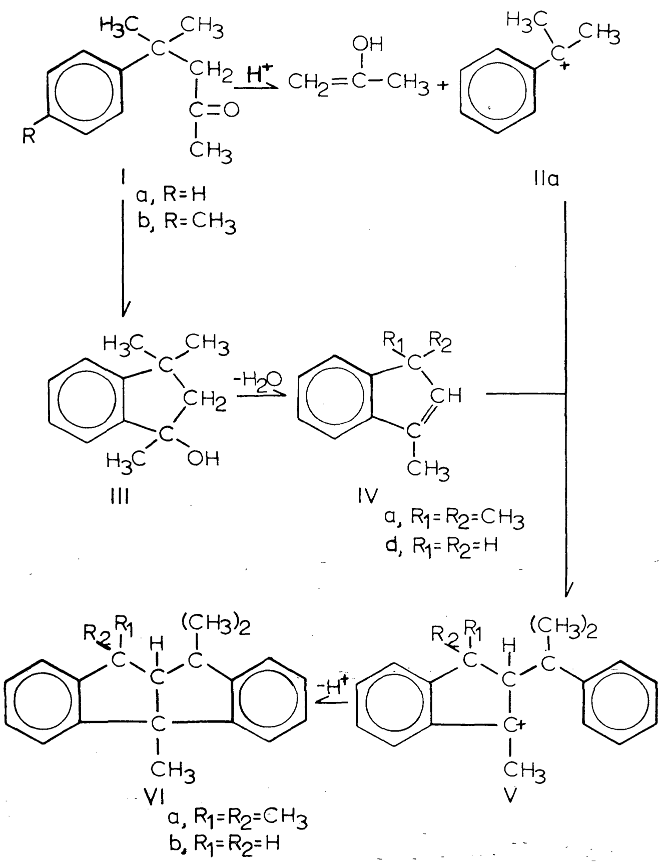
[1] *Presented in part before the Division of Petroleum Chemistry, Symposium on Aromatic Compounds at the 142nd meeting of the American Chemical Society, Atlantic City, September 1962.*

[2] *Recipient of a National Research Council Studentship.*

**This mechanism has also been independently proposed by R. A. Barnes, private communication.*

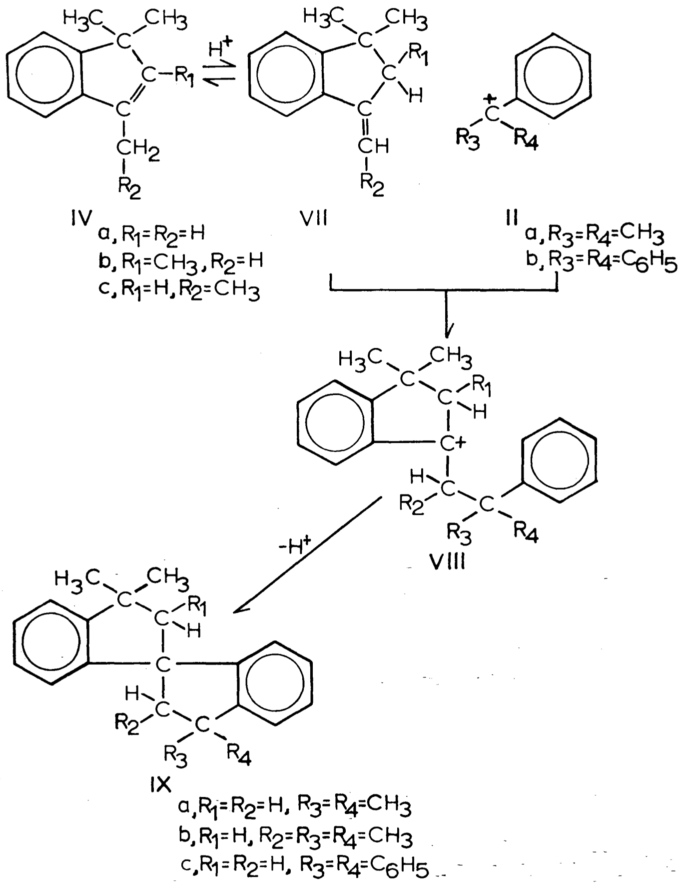
CHART I



reagents.) This equilibrium is expected to favor the endocyclic form. However, the relatively bulky protonated α-methylstyrene (either formed as shown in Chart I or added as α-methylstyrene) can alkylate the exocyclic form more readily than the hindered endocyclic form. When alkylation occurs, it causes a continual shift in the endocyclic–exocyclic equilibrium because of removal of the exocyclic form as the new carbonium ion (VIII). This carbonium ion has the charge suitably situated to alkylate the second aromatic ring producing the 3,3,3′,3′-tetramethyl-1,1′-spirobiindane (IX*a*).

To substantiate the above mechanism we found that the indene (IV*a*) reacted with α-methylstyrene in sulphuric acid to produce the 1,1′-spirobiindane (IX*a*) in 54% yield. The product has identical physical properties to that prepared by Barnes and Adams. The n.m.r. spectrum of the compound (Fig. 1) was interesting. It showed a complicated multiplet integrating for 8 aromatic protons, a singlet at 7.72 p.p.m. for the 4 methylene protons, and a doublet at 8.61 and 8.65 p.p.m. corresponding to 12 methyl protons. The aromatic proton multiplet was divided into two signals one with maximum intensity at 2.89 p.p.m. (corresponding to 6 protons) and another at 3.30 p.p.m. (corresponding to 2 protons). The examination of a molecular model helped to clarify several points about the spectrum. A possible explanation of the two groups of partially resolved multiplets in the aromatic proton signal is based on the fact that the conformation of the molecule places

CHART II

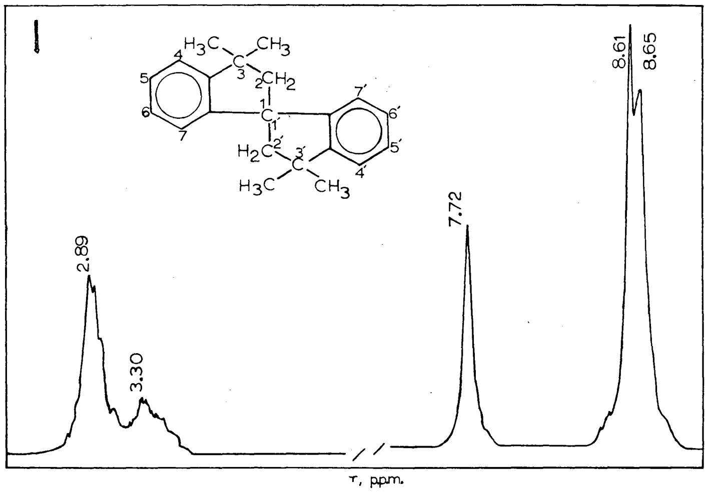


the two aromatic rings nearly at right angles to one another and reasonably close together. In such a situation the proton on carbon 7 (and 7′) would lie in a position more or less over the plane of the ring to which it was not directly attached. Thus it would be shielded and would resonate at higher field than the other aromatic protons, that is, near 3.30 p.p.m.

The fact that the methyl proton resonance is a doublet can be attributed to the fact that one of the methyl groups of each of the *gem* dimethyl systems on carbons 3 and 3′ lies in the plane of the aromatic ring to which it is less closely attached while the remaining methyl group lies slightly above the plane of the ring to which it is more closely attached. In such a situation, the group in the plane of the ring would be expected to be deshielded relative to the other group and thus resonate at slightly lower field.

On closer examination of the proposed reaction mechanism, it is obvious that any effect which tends to stabilize the endocyclic form of the indene would tend to prevent the formation of the 1,1′-spirobiindane system while any effect which tends to stabilize the exocyclic form would have the opposite effect.

With the former effect in mind, 1,1,2,3-tetramethylindene (IV*b*) was prepared. In such a system the methyl group on carbon 2 should tend to stabilize the double bond in the endocyclic form and one would expect less 1,1′-spirobiindane to form in a reaction of this indene with α-methylstyrene than was produced under similar conditions with



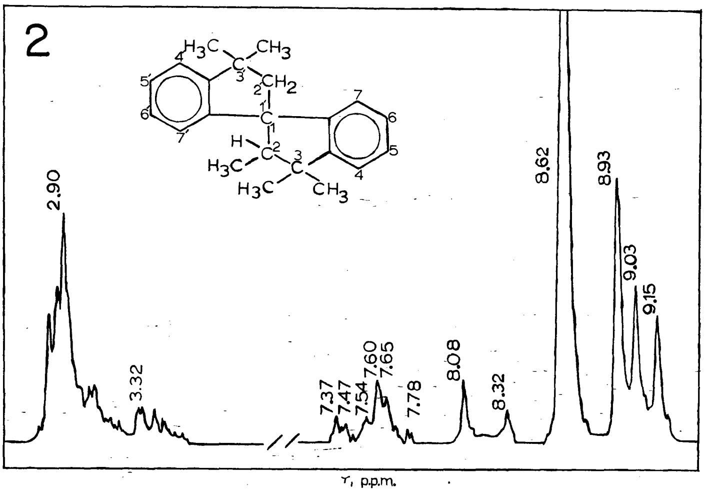


FIG. 1. Nuclear magnetic resonance spectrum of 3,3,3′,3′-tetramethyl-1,1′-spirobiindane.
FIG. 2. Nuclear magnetic resonance spectrum of 2,3,3,3′,3′-pentamethyl-1,1′-spirobiindane.

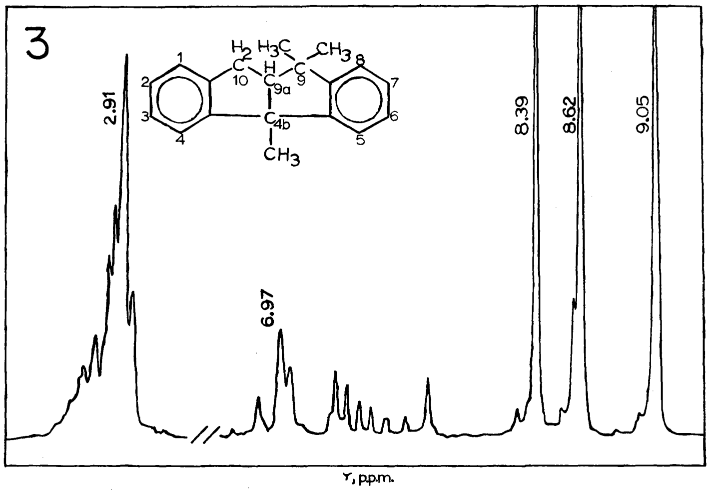
1,1,3-trimethylindene and α-methylstyrene. When the indene (IV*b*) and α-methylstyrene were reacted with sulphuric acid at −5° none of the 2,3,3,3′,3′-pentamethyl-1,1′-spirobiindane (IX*b*) was produced. The only high molecular weight compound formed was the saturated cyclic dimer of α-methylstyrene which under the conditions used does not react further to produce (IX*a*).

In order to test the stabilizing effect of an additional methyl group on the exocyclic form of an indene, 3,3-dimethyl-1-ethylindene (IV*c*) was prepared. In such a compound the exocyclic form would be expected to be more stable than in 1,1,3-trimethylindene. Reaction of the indene (IV*c*) with α-methylstyrene in sulphuric acid produced a colorless crystalline solid (m.p. 118–119°) in 67% yield. The ultraviolet spectrum gave bands at 2730 Å (log $\epsilon = 3.33$), 2660 Å (log $\epsilon = 3.29$), and 2590 Å (log $\epsilon = 3.08$). The infrared spectrum gave a doublet in the 1385–1365 cm^{-1} region attributed to the *t*-butyl skeleton and two strong bands at 765 and 750 cm^{-1} attributed to *o*-disubstituted aromatics. The mass spectrum showed a parent mass of 290. The analytical results agreed with the formula $C_{22}H_{26}$. This evidence indicated the compound was the 2,3,3,3′,3′-pentamethyl-1,1′-spirobiindane (IX*b*). The n.m.r. spectrum (Fig. 2) was complex but confirmed this. The eight aromatic protons absorbed as a complex multiplet with maximum intensities of the two separate branches at 2.90 and 3.32 p.p.m. respectively. The signals at 3.32 p.p.m. were again attributed to the shielding effect on the protons at carbons 7 and 7′ causing them to resonate at higher fields as they did in compound (IX*a*). An AB type quartet at 7.37, 7.60, 8.08, and 8.32 p.p.m. was attributed to the methylene protons of carbon 2′. These protons are not equivalent because of the interaction of one of them with the methyl group on carbon 2 which actually lies very close to it. A quartet at 7.47, 7.54, 7.65, and 7.78 p.p.m. was attributed to the methine proton on carbon 2. The quartet is a result of its spin–spin coupling with the protons of the methyl group and thus represents the methine proton's contribution to the AB_3 system. A doublet at 9.03 and 9.15 p.p.m. was attributed to the methyl protons attached to carbon 2. It formed the remainder of the AB_3 system. The singlet at 8.93 p.p.m. was attributed to one of the methyl groups on carbon 3 which appears at higher field than the other because of the shielding effect of the methyl group on the adjacent carbon 2. The singlet at 8.62 p.p.m. was attributed to the protons of the remaining three methyl groups on carbon 3 and 3′. It is interesting to note that this is not resolved as a doublet as was observed for IX*a* perhaps, because the signal of the three methyl protons on carbon 3′ that lie in the plane of the non-adjacent aromatic ring is only half as intense as that of the six methyl protons on carbons 3 and 3′ out of the plane of the adjacent aromatic rings, and is thus not resolved from the larger signal considering that the shift for two such groups in compound (IX*a*) was only 0.04 p.p.m.

Positive evidence in favor of the proposed mechanism is given by the non-reactivity of 1,1,2,3-tetramethylindene (IV*b*) with α-methylstyrene, and the fact that 3,3-dimethyl-1-ethylindene (IV*c*), in a reaction similar to the one in which compound (IX*a*) was produced from 1,1,3-trimethylindene (IV*a*) and α-methylstyrene, gave the expected product (IX*b*) in higher yield.

Several questions arise concerning the generality of these reactions. It was desirable to determine if an unhindered endocyclic form of an indene (Chart I, IV*d*) would alkylate even if an exocyclic form could exist. If the reaction producing the spirobiindanes is a general one, other suitable olefins and other alkylating agents (besides α-methylstyrene) should enter into the reaction. In attempts to investigate the generality of these reactions, further work was undertaken as described below.

The reaction of 1-methylindene with α-methylstyrene in sulphuric acid yielded a colorless liquid in 50% yield. The ultraviolet spectrum of this product gave bands at 2730 Å (log $\epsilon = 3.22$), 2660 Å (log $\epsilon = 3.25$), and 2600 Å (log $\epsilon = 3.06$). The infrared spectrum gave a doublet at 1390 and 1385 cm^{-1} attributed to the *t*-butyl skeleton, as well as a strong band at 760 cm^{-1} indicating *o*-disubstituted aromatics. The analytical results agreed with a formula $C_{19}H_{20}$ which was substantiated by the mass spectrum which indicated a parent mass of 248. The n.m.r. spectrum (Fig. 3) consisted of a multiplet of maximum intensity at 2.91 p.p.m. corresponding to 8 protons, a series of 10 signals between 6.70 and 7.66 p.p.m. integrating for 3 protons and three singlets at 8.39, 8.62, and 9.05 p.p.m. corresponding to 3 protons each. On the basis of this spectrum, the compound was apparently not a 1,1′-spirobiindane but the 4*b*,9,9-trimethyl-4*b*,9,9*a*,10-tetrahydroindeno[1,2-*a*]indene (VI*b*). This product would form if the protonated α-methylstyrene (II*a*) alkylated the 1-methylindene (IV*d*) at carbon 2 and subsequent reaction



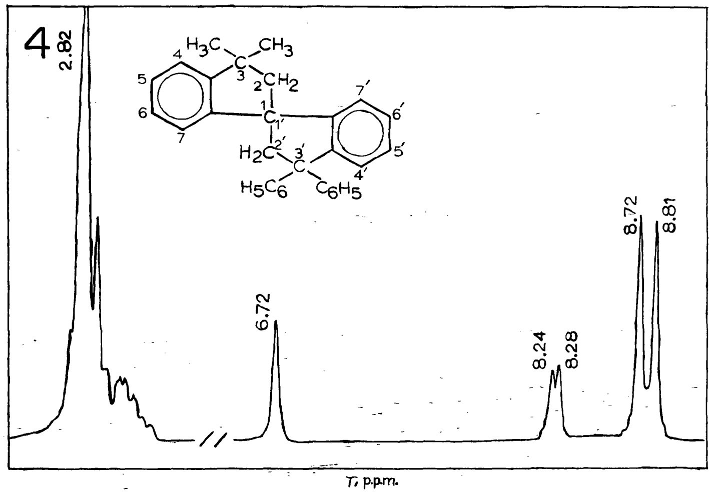


FIG. 3. Nuclear magnetic resonance spectrum of 4*b*,9,9-trimethyl-4*b*,9,9*a*,10-tetrahydroindene[1,2-*a*] indene.

FIG. 4. Nuclear magnetic resonance spectrum of 3,3-dimethyl-3′,3′-diphenyl-1,1′-spirobiindane.

followed the mechanism outlined in Chart I. The multiple signal in the n.m.r. between 6.70 and 7.66 p.p.m. was attributed to an ABC or ABX system consisting of the methine proton on carbon 9*a* and the methylene protons on carbon 10. The singlet at 8.39 p.p.m. was apparently due to one of the methyl groups on carbon 9, which, because of its position relative to the two aromatic rings, is deshielded. The singlet at 8.62 p.p.m. was then attributed to the other methyl group on carbon 9 while that at 9.05 p.p.m. was associated with the protons of the group on carbon 4*b* which, because of the type of fusion along the carbon 4*b* to carbon 9*a* bond, lie well away from either of the aromatic rings and thus resonate at higher field.

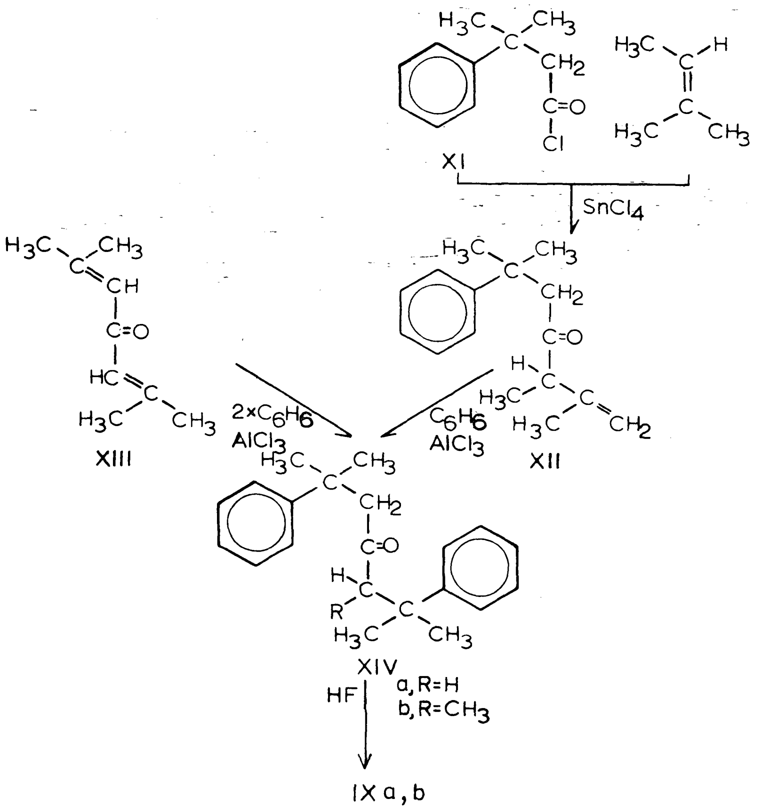
The product from the reaction of 1,1,3-trimethylindene (IV*a*) with triphenylcarbinol in sulphuric acid was a crystalline solid, m.p. 171–173° (41% yield). The ultraviolet spectrum gave bands at 2733 Å (log $\epsilon = 3.19$), 2663 Å (log $\epsilon = 3.31$), and a slight inflection at 2610 Å (log $\epsilon = 3.21$). The infrared spectrum gave strong bands at 768, 755, and

702 cm^{-1} indicative of both *o*-disubstituted and monosubstituted aromatics. The mass spectrum showed a parent mass of 400. This was substantiated by an analytical result which agreed with the molecular formula $C_{31}H_{28}$. This evidence suggested the compound was the expected 3,3-dimethyl-3′,3′-diphenyl-1,1′-spirobiindane (IX*c*). This was substantiated by the n.m.r. spectrum (Fig. 4) which gave an 18 proton multiplet at 2.82 p.p.m. A singlet at 6.72 p.p.m. integrating for 2 protons was attributed to the methylene protons on carbon 2′ which are deshielded by the adjacent aromatic ring attached to carbon 3′. A doublet at 8.24 and 8.28 p.p.m. integrated for 2 protons and was attributed to the methylene protons on carbon 2. The two methyl groups on carbon 3 gave signals at 8.72 and 8.81 p.p.m. respectively. The chemical shift of one of the methyl groups to lower field is attributed to that methyl group being in the plane of an aromatic ring as it was in compound IX*a*. The fact that the shift is greater in this case than was observed for compound IX*a* is attributed to the fact that a buttressing effect of the two bulky phenyl groups on carbon 3′ causes the other aromatic ring attached to that carbon to approach the methyl group on carbon 3 more closely than in compound IX*a* with the result that it is significantly more shielded.

As proof of the structures of two of the compounds prepared, namely, the 3,3,3′,3′-tetramethyl (IX*a*) and the 2,3,3,3′,3′-pentamethyl-1,1′-spirobiindane (IX*b*), these compounds were synthesized by unequivocal methods as outlined in Chart III.

The synthesis of (IX*a*) was realized by first treating benzene with phorone (XIII) in

CHART III



the presence of aluminum chloride to produce the 2,6-dimethyl-2,6-diphenyl-4-heptanone (XIV*a*) reported by Colonge and Pichat (6) in 70% yield. This compound had the expected n.m.r. spectra. Cyclization of this ketone with anhydrous hydrogen fluoride yielded (IX*a*) in 78% yield.

The synthesis of the 2,3,3,3′,3′-pentamethyl-compound (IX*b*) was carried out by first treating 3-methyl-3-phenylbutanoyl chloride (XI) with 2-methyl-2-butene and stannic chloride to yield 2,3,6-trimethyl-6-phenyl-1-heptene-4-one (XII). Reaction of this with benzene and aluminum chloride furnished 2,3,6-trimethyl-2,6-diphenyl-4-heptanone (XIV*b*). Treatment of this ketone with hydrogen fluoride yielded (IX*b*) identical with the (IX*b*) from the reaction of 3,3-dimethyl-1-ethylindene with α-methylstyrene.

EXPERIMENTAL

Apparatus and Methods

The ultraviolet spectra were recorded on a Beckman DK-2 ratio recording spectrophotometer using spectro grade cyclohexane as solvent. The infrared spectra were recorded on a Perkin–Elmer Model 137 "Infracord" spectrophotometer. Gas–liquid chromatography analyses were carried out on a Perkin–Elmer 154-D vapor fractometer or on an F & M Model 500 programmed temperature gas chromatograph equipped with a dual column attachment. Small samples of pure compounds were obtained by repetitive chromatography of a mixture followed by collection of pure components. The mass spectrometer analyses were done at an independent laboratory. Nuclear magnetic resonance spectra were recorded at the National Research Council, Halifax, Nova Scotia, on a Varian A-60 spectrometer using tetramethylsilane as internal standard and carbon tetrachloride as solvent. Melting points were determined on a Fischer–Johns melting point apparatus equipped with a microscope or on a Thomas–Hoover "Unimelt" capillary melting point apparatus. Reactions with anhydrous hydrogen fluoride were carried out in a 12-in. stainless steel MD test tube reactor equipped with stainless steel gaskets made by Autoclave Engineers Inc. Ultimate analyses were determined by Dr. E. Thommen, Basel, Switzerland and Dr. C. Daessle, Montreal.

Preparation of 1,1,3-Trimethylindene (IVa)

Benzene (800 ml) and aluminum chloride (360 g) were mixed at room temperature. Mesityl oxide (200 ml) was added dropwise to the stirred mixture over 45 minutes without external cooling. After 4 hours at room temperature, the mixture was hydrolyzed on ice. The organic material was separated and the aqueous layer was extracted with benzene. The combined organic layer and benzene extract were washed with 10% sodium carbonate, water, and dried over sodium sulphate. The solvent was distilled and the residue was further distilled *in vacuo* yielding 14.08 g of 1,1,3-trimethylindene, b.p. 50° at 0.65 mm, $n_D^{25} = 1.5346$ (literature (7), $n_D^{25} = 1.5346$), and 40.37 g of 4-methyl-4-phenyl-2-pentanone, b.p. 78–81° at 0.85 mm. Gas–liquid chromatography of the two products on an 8 ft silicone gum rubber column showed they were pure.

3,3,3′,3′-Tetramethyl-1,1′-spirobiindane (IXa)

The procedure for preparing IX*a* was essentially that of Barnes (2) except that phenyldimethylcarbinol was replaced by α-methylstyrene. The sulphuric acid catalyzed reaction between 1,1,3-trimethylindene (5 g, 0.031 mole) and α-methylstyrene (3.6 g, 0.031 mole) yielded 5.5 g of crude solid shown to be 81% compound IX*a* (a 54% yield) and 19% the saturated cyclic dimer of α-methylstyrene by gas–liquid chromatography.

The compound IX*a*, after recrystallization from methanol, had a melting point of 133–134° (literature (1) 133–134°). The ultraviolet spectrum gave bands at 2730 Å ($\log \epsilon = 3.12$), 2660 Å ($\log \epsilon = 3.05$), and 2595 Å ($\log \epsilon = 2.99$). This compound proved to be identical, by mixed melting point and infrared spectra, with the hydrocarbon prepared directly from 4-methyl-4-phenyl-2-pentanone according to the procedure of Hoffman (1). The infrared spectrum was identical with that reported by Adams and co-workers (3). The n.m.r. spectrum gave an 8-proton multiplet at 2.89 and 3.30 p.p.m., a 4-proton singlet at 7.72 p.p.m., and a 12-proton doublet at 8.61 and 8.65 p.p.m. The mass spectrum showed a parent mass of 276.

Preparation of 1,1,2,3-Tetramethylindene (IVb)

(a) Preparation of 3,4-Dimethyl-3-pentene-2-one

Acetyl chloride (55.75 g, 0.71 mole) and 2-methyl-2-butene, b.p. 38–41° (76.6 g, 1.09 mole), were reacted with anhydrous stannic chloride (7.1 g) according to the procedure of Colonge (8). The olefin and the acid chloride were cooled in ice and salt and the stannic chloride was added dropwise while the temperature was maintained below 0°. The mixture was then allowed to warm slowly to room temperature and finally was heated at 60–80° for 2 hours and allowed to cool slowly.

After hydrolysis on ice, extraction with ether, and washing the ether extract free of acid and drying, the solvent was distilled. Distillation of the residual liquid yielded 41.14 g of colorless liquid, b.p. 148–150°

(with the evolution of a great deal of hydrogen chloride) $n_D^{14} = 1.4491$ (literature (8), $n_D^{14} = 1.4506$). Gas–liquid chromatography showed a 99% pure product.

(b) Preparation of 1,1,2,3-Tetramethylindene

Twenty-eight grams (0.25 mole) of 3,4-dimethyl-3-pentene-2-one was cooled below 0° and hydrogen chloride (10 g) 0.27 mole, was bubbled in, thus forming the 4-chloro-3,4-dimethyl-2-pentanone. This was added dropwise to a stirred mixture of benzene (100 ml, 1.15 mole) and aluminum chloride (50 g, 0.37 mole) while the temperature was maintained at 0–10°. After it was stirred for an additional 3 hours in the cold, the mixture was hydrolyzed on ice and hydrochloric acid. The organic layer was separated, washed free of acid, and dried over sodium sulphate. Distillation yielded 19.96 g of 1,1,2,3-tetramethylindene, b.p. 76–82° at 1.6 mm, $n_D^{25} = 1.5384$ (literature (9), $n_D^{25} = 1.5431$.

Reaction of 1,1,2,3-Tetramethylindene with α-Methylstyrene

The 1,1,2,3-tetramethylindene (5.30 g, 0.031 mole) and α-methylstyrene (3.6 g, 0.031 mole) were cooled to −5° in ice and salt. Sulphuric acid (41 ml) was added dropwise with vigorous stirring as described above. After the procedure was repeated as for 1,1,3-trimethylindene, distillation of the solvent yielded 3.66 g of viscous liquid. Gas–liquid chromatography showed it to be mostly the saturated cyclic dimer of α-methylstyrene with no higher boiling material.

Preparation of 3,3-Dimethyl-1-ethylindene (IVc)

(a) 3,3-Dimethyl-1-indanone

3-Methyl-3-phenylbutanoic acid, prepared by the alkylation of benzene with 3-methyl-2-butenoic acid (10), had a melting point of 55–57° (literature (11), m.p. 58–59°). This acid was converted to 3,3-dimethyl-1-indanone according to the procedure of Koelsch and Le Clair (11).

(b) Preparation of 3,3-Dimethyl-1-ethylindene

A Grignard reagent was prepared from 4.86 g (0.045 mole) of ethyl bromide and 0.72 g (0.032 mole) of magnesium in 30 ml of anhydrous ethyl ether. Crude 3,3-dimethyl-1-indanone (from part *a*) (4.31 g, 0.026 mole) in 15 ml of ether was added to the reagent over 45 minutes while the temperature was maintained at 0–5°. The mixture was then refluxed for 2 hours and hydrolyzed on ice. The crude product isolated by extraction with ether was refluxed for 2 hours with 10% aqueous oxalic acid and the oil obtained by ether extraction was chromatographed from petroleum ether on alumina. The first fraction from the alumina column yielded 1.71 g of an oil which was mainly the desired indene according to the similarity of its ultraviolet and infrared spectra with those of 1,1,3-trimethylindene. There was a slight contamination with the starting ketone as shown by a weak band for carbonyl absorption at 1700 cm^{-1}.

2,3,3,3′,3′-Pentamethyl-1,1′-spirobiindane (IXb)

The 3,3-dimethyl-1-ethylindene (0.50 g, 0.0029 mole) and α-methylstyrene (0.34 g, 0.0029 mole) were cooled to −15° and sulphuric acid (5.0 g) was added as described before. Distillation of the solvent after completion of the reaction and extraction with petroleum ether yielded 0.52 g of solid. Gas–liquid chromatography indicated that the major component (90%) was not compound IX*a* but a higher boiling one. The solid was fractionally sublimed *in vacuo*. Recrystallization of the fractions from absolute ethanol yielded colorless crystals, m.p. 118–119°. The ultraviolet spectrum gave bands at 2730 Å (log $\epsilon = 3.33$), 2660 Å (log $\epsilon = 3.29$), and 2590 Å (log $\epsilon = 3.08$). The infrared spectrum gave a doublet in the 1385–1365 cm^{-1} region attributed to the *t*-butyl structure and two bands of equal intensity at 765 and 750 cm^{-1} attributed to *o*-disubstituted aromatics. The n.m.r. spectrum showed an 8-proton multiplet with maximum intensities at 2.90 and 3.32 p.p.m., a 2-proton quartet at 7.37, 7.60, 8.08, and 8.32 p.p.m., a single proton quartet at 7.47, 7.54, 7.65, and 7.78 p.p.m., a 3-proton singlet at 8.93 p.p.m., a 3-proton doublet at 9.03 and 9.15 p.p.m., and a 9-proton singlet at 8.62 p.p.m. The mass spectrum indicated a parent mass of 290. Analysis—Found: C, 90.30, 90.38; H, 9.31, 9.29. Calculated for $C_{22}H_{26}$: C, 90.98; H, 9.02.

4b,9,9-Trimethyl-4b,9,9a,10-tetrahydroindeno-[1,2a]-indene (VIb)

The 1-methylindene was prepared following the procedure of Stoermer and Laage (12) using the modification of Parham and co-workers (13). The product distilled at 84° at 11 mm, $n_D^{25} = 1.5630$ (literature (13), b.p. 76–78° at 11 mm, $n_D^{25} = 1.5587$) yielding 7.63 g of 1-methylindene.

The 1-methylindene (0.78 g, 0.006 mole) and the α-methylstyrene (0.71 g, 0.006 mole) were reacted with sulphuric acid as described above to yield 0.66 g of viscous liquid. Gas–liquid chromatography on a silicone grease column showed it to be 12% the saturated cyclic dimer of α-methylstyrene and 62% a compound which was not IX*a*. An attempt to separate the major component by molecular distillation was unsuccessful. Small samples were then repeatedly chromatographed on the F & M Model 500 and the compound collected as a colorless liquid. The ultraviolet spectrum gave bands at 2730 Å (log $\epsilon = 3.22$), 2660 Å (log $\epsilon = 3.25$), and 2600 Å (log $\epsilon = 3.06$). The infrared spectrum gave a doublet at 1390 and 1385 cm^{-1} characteristic of a *t*-butyl group and also showed a strong band at 760 cm^{-1} for *o*-disubstituted aromatics. The mass spectrum showed a parent mass of 248. The n.m.r. spectrum gave an 8-proton multiplet at 2.91 p.p.m., a complex 3-proton 10-band ABC or ABX multiplet between 6.70 and 7.66 p.p.m., and three

3-proton singlets at 8.39, 8.62, and 9.05 p.p.m. Analysis—Found: C, 91.07, 90.92; H, 8.11, 8.07. Calculated for $C_{19}H_{20}$: C, 91.54; H, 8.46.

3,3-Dimethyl-3′,3′-diphenyl-1,1′-spirobiindane (IXc)

The 1,1,3-trimethylindene (1.0 g, 0.006 mole) and triphenylcarbinol (1.56 g, 0.006 mole) were reacted with 8 ml of sulphuric acid as described above. After 2 hours' stirring the temperature had risen to 10°. The mixture was extracted with benzene after standing overnight at room temperature. Subsequent washing, drying, and distillation of the solvent yielded 1.0 g (41% yield) of solid. The solid was chromatographed from benzene on alumina to yield a thick oil which crystallized on treatment with acetone. Recrystallization from acetone yielded colorless crystals, m.p. 171–173°. The ultraviolet spectrum gave bands at 2733 Å ($\log \epsilon = 3.19$), 2663 Å ($\log \epsilon = 3.31$), and an inflection at 2610 Å ($\log \epsilon = 3.21$). The infrared spectrum showed strong bands at 768, 755, and 702 cm^{-1} apparently due to both *o*-disubstituted and monosubstituted aromatics. The mass spectrum showed a parent mass of 400. The n.m.r. spectrum showed an 18-proton multiplet at 2.82 p.p.m., a 2-proton singlet at 6.72 p.p.m., a 2-proton doublet at 8.24 and 8.28 p.p.m., and two 6-proton singlets at 8.72 and 8.81 p.p.m. Analysis—Found: C, 92.83, 92.90; H, 7.08, 7.20. Calculated for $C_{31}H_{28}$: C, 92.95; H, 7.04.

Synthesis of 3,3,3′,3′-Tetramethyl-1,1′-spirobiindane (IXa)

(a) Preparation of 2,6-Dimethyl-2,6-diphenyl-4-heptanone (XIVa)

Benzene (64 g, 0.82 mole) and aluminum chloride (26.0 g, 0.27 mole) were cooled to 15–20°. Phorone (27.6 g, 0.20 mole) was added with stirring over 45 minutes at 15–20°. The mixture was stirred for 4 hours and allowed to stand for 43 hours at room temperature. After hydrolysis on ice, extraction, drying, and distillation of the solvent, the residue was distilled to yield 41.5 g of the desired ketone, b.p. 158–160° at 0.45 mm, $n_D^{19} = 1.5462$ (literature (6), $n_D^{17} = 1.5465$). The infrared spectrum indicated a monosubstituted aromatic ketone. The carbonyl absorption appeared at 1700 cm^{-1} and two strong bands at 700 cm^{-1} and 830 cm^{-1} were attributed to a monosubstituted aromatic. The ultraviolet spectrum gave bands at 2640 Å ($\log \epsilon = 2.70$), 2585 Å ($\log \epsilon = 2.77$), and 2535 Å ($\log \epsilon = 2.71$). The n.m.r. spectrum gave a 10-proton singlet at 2.95 p.p.m., a 4-proton singlet at 7.73 p.p.m., and a 12-proton singlet at 8.76 p.p.m.

(b) Reaction of 2,6-Dimethyl-2,6-diphenyl-4-heptanone with Hydrogen Fluoride

The hydrogen fluoride (10.0 g) was condensed in the cold reactor tube. The ketone (9.11 g, 0.031 mole) was added rapidly. The tube was sealed and stirred for 24 hours. It was then cooled and opened. The contents were solid. Petroleum ether was added to dissolve the solid. The ether extract was washed free of acid with water and dried. Distillation of the solvent yielded 7.35 g of solid. Gas–liquid chromatography on a 2-m silicone grease column indicated the solid was 89% compound IX*a* (75% yield). Recrystallization from methanol gave colorless needles, m.p. 135–136°. A mixed melting point and infrared spectrum showed this product to be identical with IX*a* produced from 1,1,3-trimethylindene and α-methylstyrene.

Synthesis of 2,3,3,3′,3′-Pentamethyl-1,1′-spirobiindane (IXb)

(a) Preparation of 2,3,6-Trimethyl-6-phenyl-1-heptene-4-one (XII)

Ten grams (0.051 mole) of 3-methyl-3-phenylbutanoyl chloride and 2-methyl-2-butene (4.68 g, 0.068 mole) were cooled below −5°. Anhydrous stannic chloride (1.5 g) was added dropwise with stirring while the temperature was maintained below 0°. The mixture was then allowed to warm slowly to room temperature. After 7 hours, the reaction was hydrolyzed on ice. After extraction with benzene, washing, drying, and distilling the solvent, the residual liquid distilled at 120° at 1.8 mm yielding 6.88 g of a colorless liquid. Gas–liquid chromatography indicated two components which were found by infrared and ultraviolet spectra to be the two isomeric olefins possible. The infrared spectrum of the major component showed carbonyl absorption at 1700 cm^{-1} and a strong band at 900 cm^{-1} attributed to out-of-plane deformations of the protons of the terminal methylene group of XII. The ultraviolet spectrum of this component showed fine structure in the absorption at 2640, 2585, and 2525 Å typical of a substituted (non-conjugated) aromatic compound. On the other hand, the ultraviolet spectrum of the minor component separated on the chromatograph showed a broad band at 2400–2420 Å, presumably indicative of the conjugated isomer of XII.

(b) Preparation of 2,3,6-Trimethyl-2,6-diphenyl-4-heptanone (XIVb)

Benzene (4.68 g, 0.06 mole) and aluminum chloride (2.66 g, 0.020 mole) were mixed and cooled to 5–10°. The 2,3,6-trimethyl-6-phenyl-1-heptene-4-one (3.44 g, 0.015 mole) was added over 30 minutes while the temperature was maintained by cooling. The mixture was allowed to warm slowly to room temperature. Gas–liquid chromatography of an aliquot after 3 hours indicated little starting olefin. The mixture was hydrolyzed at once on ice. After the usual extraction and subsequent treatment, the residue distilled at 172–174° at 0.8 mm to yield 2 g of a viscous yellow oil, $n_D^{17} = 1.5460$. The product showed strong carbonyl absorption at 1700 cm^{-1}, lacked the olefinic proton absorption of the starting material at 900 cm^{-1}, and was generally very similar to the spectrum of 2,6-dimethyl-2,6-diphenyl-4-heptanone. Analysis—Found: C, 86.35; H, 9.35. Calculated for $C_{22}H_{28}O$: C, 85.66; H, 9.12.

(c) Reaction of 2,3,6-Trimethyl-2,6-diphenyl-4-heptanone with Hydrogen Fluoride

The hydrogen fluoride (10 g) was condensed in the cooled reactor. The ketone (1.0 g, 0.003 mole), dissolved in 6 ml of carbon tetrachloride, was added rapidly. The tube was sealed, stirred for 1 hour, and allowed to stand for 8 hours at room temperature. After the reactor was cooled and opened in the usual way, the contents were poured on ice. Subsequent treatment yielded 0.90 g of solid. Gas–liquid chromatography of this on an 8-ft silicone gum rubber column showed four components with the major one having a retention time identical with that of a sample of IX*b*. Recrystallization from ethanol yielded a colorless crystalline solid, m.p. 116–119°. A mixed melting point with a sample of IX*b* from the reaction of 3,3-dimethyl-1-ethylindene with α-methylstyrene showed no depression. The infrared spectra of the two samples were identical.

ACKNOWLEDGMENTS

The authors wish to thank Dr. G. McInnes of the National Research Council, Halifax, Nova Scotia, for recording the n.m.r. spectra. Financial assistance from the National Research Council is gratefully acknowledged.

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