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Proton-Mobility in the Indene Ring-System

IV *. Alkyl-Substituted Indenes; their Syntheses, Structures and Tautomeric Rearrangements

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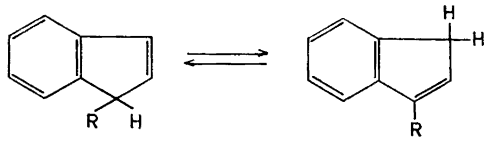
Various synthetic methods for the preparation of 1- and 3-substituted indenes have been investigated. The definite structures of the indenes were determined by NMR-spectroscopy. The base-catalyzed tautomeric rearrangement was studied by the same technique.

Our current investigations [1,2] on the proton-mobility in the five-membered ring of indene, required the syntheses and structure determinations of a certain number of alkylsubstituted indenes. Due to the tautomerism in the five-membered ring, there are two possible structures for monosubstituted indenes:



There has been much discussion in the literature, as to whether these two tautomeric compounds can exist separately. 1- (or 3-) ** alkylindenes have been described several times, but in each case no unambiguous structural proofs, based on chemical facts, were given. Methylindene was first prepared from 3-methylindene-2-carboxylic acid by decarboxylation;[3] the procedure was expected to give 3-methylindene. In 1900 Marckwald [4] applied a new method for preparing monosubstituted indenes; he heated indene with solid potassium hydroxide and an alkylhalide. Since alkylation of the indenyl-anion originally must give 1-substitution, he described the products as 1-methyl- and 1-benzylindene.

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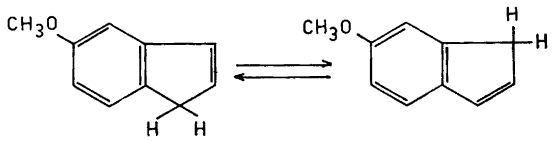
** The numbering is in accord with *Chem. Abstr.*

Some years later Thiele and Bühner [5] repeated Marckwald's work, and showed that the two tautomeric forms of methylindene and benzylindene previously described in the literature, were identical. They concluded that the double bond in the five-membered ring of indene does not have a fixed position; consequently the two described forms of alkylindenes must be identical.

A new method [6] for preparing indenylsodium with sodamide facilitated the alkylation of indene and permitted a closer study of the reaction but did not solve the tautomeric problem.

Of greater importance, however, was the work by Courtot,[7] who described a benzylindene, prepared from indenyl-magnesium bromide and benzylchloride. It was not crystalline, but when treated with alkali it gave a substance, m.p. 33—34°, which was identical with the benzylindene, previously reported.[4,5] Courtot thus claimed that he had obtained 1-benzylindene. In view of these results Wüest [8] suggested, in 1918, that monoalkylindenes mainly exist as 3-substituted compounds. If the 1-alkylindene is first formed it easily isomerizes to 3-alkylindene.

An extensive investigation of the tautomerism in three-carbon systems was carried out by Ingold and Piggott [9] during the nineteentwenties. They studied indene substituted in the six-membered ring. Methoxyindenes were synthesized by standard methods.



The two different forms could not be isolated, however, different synthetic methods giving identical products. The single substance thus isolated gave a mixture of two homophthalic acids on oxidation. By condensation with piperonal, a mixture of two derivatives was obtained. Ingold and Piggott concluded from these results that indene possesses a mobile tautomeric system, which renders it impossible to isolate two tautomeric monosubstituted indenes.

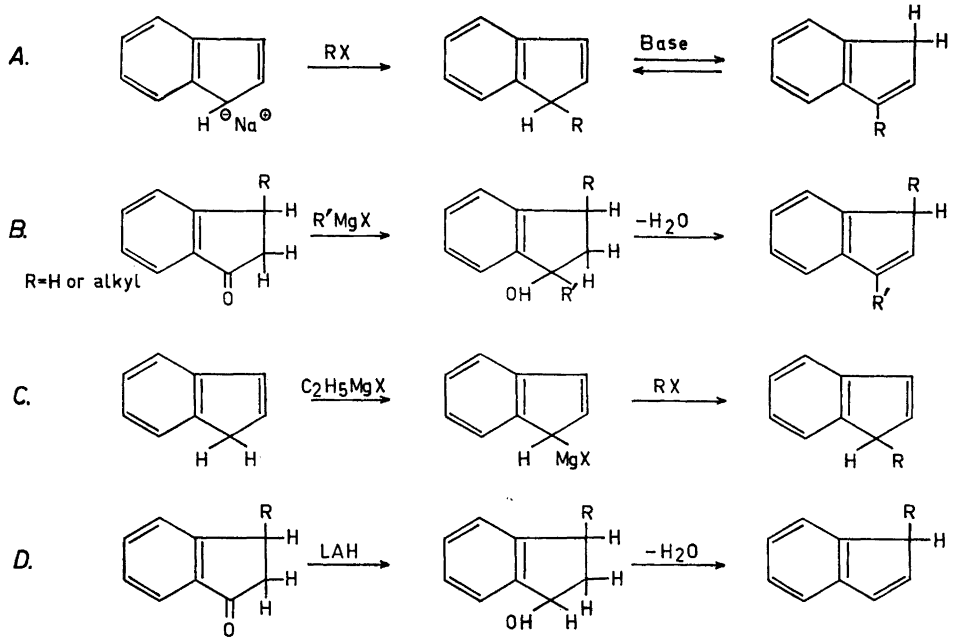
Twenty years later Koelsch and Scheiderbauer [10] succeeded in isolating two 5- and 6-substituted indenes, which did not seem to be identical. However, the theory of a mobile tautomeric system in the indene molecule was not abandoned.[11]

Recently, Elleman and Manatt [12] analyzed the NMR-spectrum of indene. They found a weak coupling between the 3-vinylic proton and one of the aromatic protons, which in fact eliminates a spontaneous rapid tautomeric rearrangement.

Also of great interest was a paper by Cristol and Plenat [13] which appeared after the present investigations had been started. They described a methylindene which, according to the synthetic route, should be 1-methylindene had no rearrangement occurred. 3-Methyl-1-indanone was reduced with lithium aluminium hydride and the alcohol obtained was dehydrated with potassium bisulphate. The structure elucidation was based on the IR-spectrum.

We have now investigated the different synthetic methods for alkylindenes, described in the literature. The structures of the substituted indenes obtained have been determined by NMR-spectroscopy.

Methods

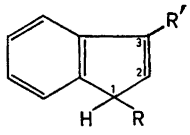


Starting with procedure A[4–6] a method was sought to convert indene quantitatively to the indenyl-anion as in many cases it was difficult to separate the alkylindene from unreacted starting material. Indene reacts only slowly with finely dispersed sodium and even sodium hydride; kept at 120° for 24 h with this latter reagent, there still remained considerable amounts of unreacted indene. However, it was found that on addition of indene to a slight excess of phenylsodium in toluene, indene was quantitatively converted to indenylsodium after a short time (30 min) at a moderate temperature. Subsequent alkylation without isolation of the intermediate product, afforded monosubstituted indene in good yields. As an alternative, butyllithium and indene also give the indenyl-anion in good yield.[14] However, having a high speed dispersing stirrer at our disposal, the preparation of phenylsodium was very simple, and the whole reaction sequence could be carried out in the same flask; the yields ranged from 60 to 72 %.

Applying this method, methyl-, benzyl- and isopropylindene were prepared.

The shifts, relative intensities and fine structures of the various proton peaks of the NMR-spectra were consistent with 3-substitution in all cases. (Table 1).

	R	R′
I	H	$-CH_3$
II	H	$-CH(CH_3)_2$
III	H	$-CH_2-C_6H_5$
IV	H	$-C(CH_3)_3$
V	$-CH_2C_6H_5$	H



	R	R′
VI	$-CH_3$	H
VII	$-CH_3$	$-C(CH_3)_3$
VIII	$-C(CH_3)_3$	$-CH_3$
IX	$-CH_3$	$-CH(CH_3)_2$
X	$-CH(CH_3)_2$	$-CH_3$

Thus, alkylation of indenylsodium first gives 1-alkylindene, which then rearranges to the 3-alkyl derivative under these conditions.

The most frequently applied synthetic method leading to alkylindenes is the treatment of 1-indanone with a Grignard reagent (method B). Although no definite structure proofs have been made, it has been assumed that 3-alkylindene is formed on dehydration of the alkyl-hydroxy-indane obtained. According to the procedure of Stoermer and Laage,[15] methylindene,[16] benzylindene and *tert*-butylindene have been prepared. The yields vary considerably depending on the Grignard reagent used; calculated on indene it is about 40 % for metylindene and benzylindene. The NMR-spectra showed 3-substitution in all cases (Table 1). Consequently, this method also gives 3-alkylindene, without any rearrangement occurring.

It was of great interest to investigate whether a 1-substituted indene could be isolated without isomerization to the 3-substituted compound. Courtot's [7] and Cristol's [13] syntheses of benzylindene and methylindene, respectively, were repeated. The NMR-spectra were not identical with those obtained for 3-methyl- and 3-benzylindene. For the methylindene thus prepared, the methyl proton peak appeared at a higher field, 1.19 ppm (δ), as compared to 2.06 ppm (δ) for 3-methyl-protons. Furthermore, the spectrum showed four bands due to non-aromatic protons with the relative intensities 1:1:1:3. Similarly the spectrum of benzylindene showed 1-substitution. Despite the fact that benzylindene gave a spectrum of the second order which has not been fully analyzed, the shifts of the vinylic protons and the CH-proton, in addition to the fine structures, unambiguously proved the structure of this compound (Table 1).

Courtot's method (C) thus gives 1-substituted indenes, the experimental conditions being sufficiently mild to permit isolation of this isomer. However, the method is limited to the use of reactive halides. Also dehydration of 1-alkyl-3-hydroxy-indane (method D) with acid reagent such as potassium bisulphate or phosphorus pentoxide gives only the 1-substituted isomer. However, prolonged heating during dehydration has been observed to cause partial rearrangement.

Starting with the optically active 3-methyl-1-indanone and applying method D, (+)-1-methylindene has also been prepared.

Having the 1-substituted indenes at our disposal, it was possible to study the rearrangement of a 1-alkylindene to the 3-alkyl-isomer. 1-Methylindene is stable in moderately acid and neutral solution, and can be stored for longer intervals in the cold under nitrogen, without decomposition. However, under the influence of a basic catalyst it rearranges completely to 3-methylindene.

Table 1.

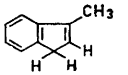
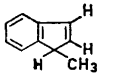
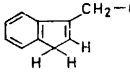
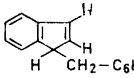
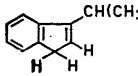
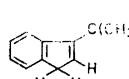
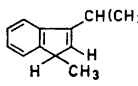
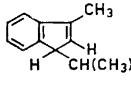
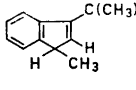
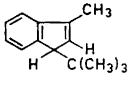
	Solvent	Shifts ppm (δ) and relative intensities ( )						Coupling constants (c/s)
		A	K	X	Methyl		Other protons	
 I	dioxane		6.04 (1)	3.13 (2)	2.06 (3)			$J_{CH_3\text{-}X} = 2.2 \pm 0.1$; $J_{KX} = 1.8 \pm 0.2$ $J_{CH_3\text{-}K} = 1.7 \pm 0.1$
 VI	dioxane	6.71 (1)	6.35 (1)	3.32 (1)		1.19 (3)		$J_{CH_3\text{-}X} = 7.6 \pm 0.2$; $J_{AX} = 1.95 \pm 0.05$ $J_{AK} = 5.7 \pm 0.1$; $J_{KX} = 1.95 \pm 0.05$
 III	acetone		6.07 (1)	3.20 (2)			CH_2 3.80 (2)	$J_{CH_2\text{-}X} = 1.8 \pm 0.1$; $J_{KX} = 1.9 \pm 0.1$ $J_{CH_2\text{-}K} = 1.8 \pm 0.1$
 V	neat	6.56 (1)	6.20 (1)	3.49 (1)			CH_2 2.2–3.0	$J_{CH_2\text{-}X} = 7.75 \pm 0.15$; $J_{AX} = 1.65 \pm 0.05$ $J_{AK} = 5.7 \pm 0.05$; $J_{KX} = 1.65 \pm 0.05$
 II	neat	5.98 (1)		3.03 (2)		1.19 (6)	CH 2.76 (1)	$J_{CH_3\text{-}CH} = 6.70 \pm 0.05$; $J_{CH\text{-}K} = 1.75 \pm 0.15$ $J_{CH\text{-}X} = 1.75 \pm 0.05$; $J_{KX} = 1.75 \pm 0.15$
 IV	neat		5.96 (1)	2.98 (2)		1.29 (9)		$J_{KX} = 2.05 \pm 0.05$

Table 1 (continued.)

 IX	neat		5.99 (1)	3.23 (1)		1,15, 1.21 (9)	CH 2.74 (1)	$J_{(CH_3)_2\text{-}CH} = 6.75 \pm 0.05$; $J_{CH\text{-}X} = 1.60 \pm 0.15$ $J_{CH\text{-}K} = 1.65 \pm 0.05$ $J_{CH_3\text{-}X} = 7.65 \pm 0.05$; $J_{KX} = 1.65 \pm 0.1$
 X	neat		6.03 (1)	3.20 (1)	2.02 (3)	0.53—1.44	CH ~ 2.10	$J_{(CH_3)_2\text{-}CH} = 6.7 \pm 0.1$; $J_{CH_3\text{-}K} = 1.6 \pm 0.1$ $J_{CH\text{-}X} = 2.4 \pm 0.1$ $J_{CH_3\text{-}X} = 2.0 \pm 0.05$; $J_{KX} = 1.7 \pm 0.1$
 VII	neat		6.01 (1)	3.19 (1)		1.13, 1.32 (3) (9)		$J_{CH_3\text{-}X} = 7.60 \pm 0.1$ $J_{KX} = 2.0 \pm 0.1$
 VIII	chloroform		6.09 (1)	3.05 (1)	1.98 (3)	0.87 (9)		$J_{CH_3\text{-}X} = 2.0 \pm 0.05$; $J_{KX} = 1.50 \pm 0.05$ $J_{CH_3\text{-}K} = 1.50 \pm 0.05$

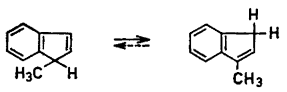
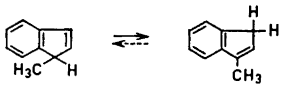
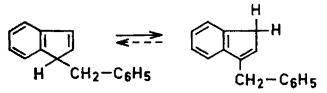
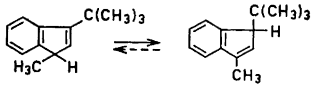
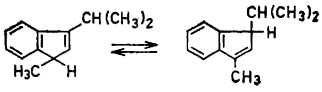
The procedure was studied kinetically by the NMR-technique, the decrease of the area under one of the vinylic proton-peaks in 1-methylindene being a criterion for the decrease in concentration of that compound. The rearrangement followed pseudo-first order kinetics and the rate constant was directly proportional to the concentration of triethylamine (TEA) used as catalyst (Table 2).

For comparative studies, the racemization of (+)-1-methylindene was determined. The preliminary results from these kinetic studies have recently been published.[1]

The isomerization of 1-benzylindene to 3-benzylindene was similarly studied kinetically, with TEA as catalyst (Table 2), (Fig. 1).

For our investigations of the peculiarities of the tautomeric indenes, a 1,3-disubstituted indene was required, which was liable to rearrange completely, or at least to a high extent to the thermodynamically more stable compound when subjected to a basic catalyst. Treatment of alkylated 1-indanone with a Grignard reagent would give a disubstituted substance, and the method would also permit synthesis of the corresponding optically active compound. Thus 1-methyl-3-*tert*-butylindene (VII) was prepared, and the structure was proven

Table 2.

$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$	Amount of A in equilibrium mixture	Catalyst	Conc. of catalyst M	$k \times 10^{-4}$ sec^{-1} pseudo-first order	$k \times 10^{-4}$ l mole^{-1} sec^{-1} second order	Fig.
	no measurable	TEA	0.257	3.0	12	Ref. 1
	—»—	TEA	0.129	1.5	12	—»—
	—»—	TEA	0.214	4.6	22	1
	no measurable	BUA	0.70	0.36	0.51	2
	20 %	BUA	1.00	1.47 ($k_1 + k_{-1}$)	1.47 ($k_1 + k_{-1}$)	3

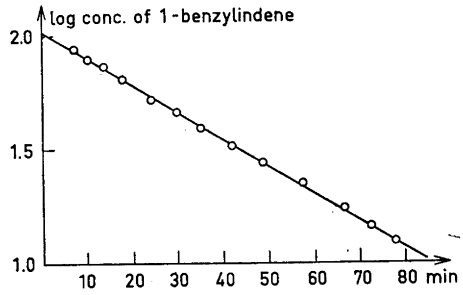


Fig. 1. Isomerization of 1-benzylindene to 3-benzylindene. $k = 4.6 \times 10^{-4}$ sec^{-1} (30°).

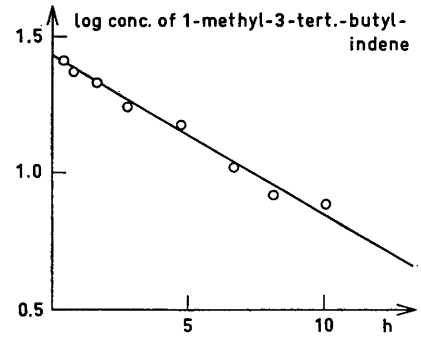


Fig. 2. Isomerization of 1-methyl-3-*tert*-butylindene to 1-*tert*-butyl-3-methylindene. $k = 3.6 \times 10^{-5}$ sec^{-1} (30°).

by means of its NMR-spectrum (Table 1). In a pyridine solution with butylamine (BUA) as catalyst, it rearranged completely to 1-*tert*-butyl-3-methylindene (VIII) (Table 2). The increase in the concentration of (VIII) was followed by the increase of the area under the methyl-proton-peak at 1.98 ppm (δ) (Fig. 2). However, the yield of the Grignard reaction was very low, and we therefore chose to investigate the properties of 1-methyl-3-isopropylindene (IX). It was prepared in the same way as (VII), and the NMR-spectrum confirmed the expected structure (Table 1).

When dissolved in pyridine and TEA at 30°, 1-methyl-3-isopropylindene showed no tendency to isomerize. On heating, however, a slow rearrangement to 3-methyl-1-isopropylindene (X) took place. Using the less bulky butylamine as catalyst, the isomerization rate at 30° was fast enough to permit convenient

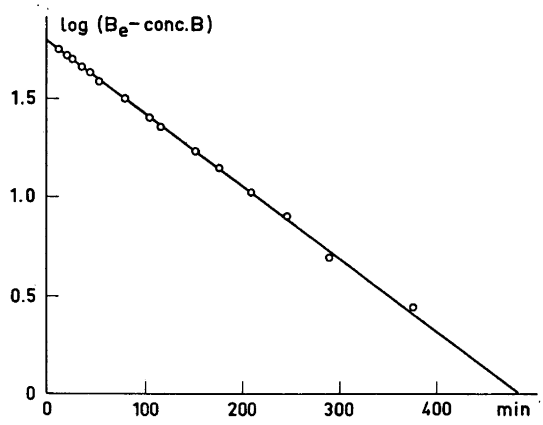


Fig. 3. Isomerization of 1-methyl-3-isopropylindene (A) to 1-isopropyl-3-methylindene (B), $A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$. Concentration of B at equilibrium: B_e. $k_1 + k_{-1} = 1.47 \times 10^{-4}$ sec^{-1} (30°).

kinetic studies. Thus a solution of 1-methyl-3-isopropylindene in pyridine and BUA reached an equilibrium at about 80 % of complete conversion to 3-methyl-1-isopropylindene. The reversible reaction followed pseudo-first order kinetics (Fig. 3) and the sum of the forward and the reverse rate constants was calculated: $k_1 + k_{-1} = 1.47 \times 10^{-4}$ sec^{-1}. The increase in the area under the methyl proton-peak at 2.02 ppm (δ) was taken as the criterion for the increase in concentration of (X) (Table 2).

Starting with optically active 3-methyl-1-indanone, (+)-1-methyl-3-isopropylindene was also obtained and studied kinetically. The preliminary results on the rearrangements have recently been published.[2]

Further kinetic investigations on optically active and racemic 1-methylindene and 1-methyl-3-isopropylindene are in progress.

EXPERIMENTAL

The NMR-spectra were obtained with a Varian A-60 high resolution spectrometer. All shifts are given as δ-values relative tetramethylsilane as the internal standard.

3-Methylindene I. (Method A). Indenylsodium: A sodium dispersion was prepared from 13.8 g (0.6 mole) of sodium in 150 ml of dry toluene by means of a "Polytron" dispersing stirrer. The dispersion was cooled to room temperature and then 10 ml of a solution of 33.7 g (0.3 mole) of freshly distilled chlorobenzene in 75 ml of toluene were added under nitrogen. A dark colour and rise in temperature indicated the start of the reaction. The rest of the chlorobenzene solution was added dropwise (60 min), occasional cooling in a dry ice-acetone bath, to keep the temperature between 20 and 40°. After complete addition, the phenylsodium was kept at room temperature for 15 min and then 29.0 g (0.25 mole) of indene in 75 ml of dry toluene were added dropwise (30 min). The mixture was heated at 75° for 2 h during which time the colour changed from black to dark red. 42.6 g (0.3 mole) of methyliodide in 75 ml of dry toluene were added to the indenylsodium and the mixture was stirred for an additional 30 min. The excess phenylsodium was decomposed by the gentle addition of 25 ml of abs. ethanol and then 100 ml of water. The toluene layer was separated, the aqueous layer acidified with dilute sulphuric acid and extracted with ether. The organic layers were combined, washed with dilute sulphuric acid and water, and dried. Evaporation of the solvent and distillation gave 3-methylindene (23.5 g, 72 %), b.p. 75–77° (10 mm), $n_D^{20} = 1.5596$; lit.[15] values: b.p. 76–78° (11 mm), $n_D^{25} = 1.5587$.

3-Isopropylindene II. According to method A described above, 3-isopropylindene was prepared from 23.2 g (0.20 mole) of indene and 0.25 mole of phenylsodium in 300 ml of dry toluene. Alkylation with 24.6 g (0.20 mole) of isopropylbromide in 50 ml of dry toluene gave 3-isopropylindene (20.0 g, 63 %) b.p. 99–101° (9.5 mm), $n_D^{22} = 1.5467$; lit.[17] values for 3-isopropylindene prepared from 1-hydrindone: b.p. 57.5° (0.55 mm), $n_D^{25} = 1.5472-1.5482$, yield 43 % calculated on 1-indanone.

3-Benzylindene III. 3-Benzylindene was prepared in two ways. *Method A:* 23.2 g (0.20 mole) of indene and 0.20 mole * of phenylsodium in 300 ml of dry toluene gave after reaction with 32.0 g (0.25 mole) of benzylchloride in toluene the expected 3-benzylindene as a yellow oil, (24.5 g, 60 %), b.p. 90–93° (0.05 mm); lit.[5] value: b.p. 183–185° (13 mm). On cooling, the substance solidified. Recrystallisation from ethanol afforded 3-benzylindene as white flakes, m.p. 32.0–32.5°; lit.[6] m.p. 33–34°.

Method B: 10.0 g (0.08 mole) of 1-indanone [18] in 50 ml of dry ether were added dropwise to an ether solution of benzyl magnesium chloride, prepared from 2.4 g (0.10 g atom) of magnesium and 12.7 g (0.10 mole) of benzyl chloride. The mixture was refluxed for 30 min and poured on to 150 ml of ice and 40 ml of 20 % sulphuric acid. After distillation of the ether, additional 40 ml of 20 % sulphuric acid were added. The mixture was heated at 100° for 15 min, cooled, and extracted with ether. The ether layer was washed

* In this case equivalent amounts of indene and phenylsodium were used to avoid reaction of benzylchloride with the excess phenylsodium.

with water and dried. Evaporation of the solvent and distillation gave 3-benzylindene (12.0 g, 77 %), b.p. 120–123° (0.4 mm). The yield calculated on indene was 43 %. The product crystallized in the cold, giving white flakes from ethanol, m.p. 32–33°.

3-tert-Butylindene IV. Analogous to the method described for benzylindene above (B), 3-*tert*-butylindene was prepared from 13.2 g (0.1 mole) of 1-indanone and 0.2 mole of *tert*-butyl magnesium chloride in 100 ml of dry ether. The resulting mixture was refluxed for 18 h and then treated with 20 % sulphuric acid. The distilled product, b.p. 105–115° (9 mm), 4.1 g, contained considerable amounts of 1-indanone, which were removed by chromatography on neutral alumina (Merck). Thus, 3.0 g of crude substance gave on elution with petroleum ether (b.p. 60–75°) 1.9 g of pure 3-*tert*-butylindene, yield 15 %, n_D^{20} = 1.5363. (Found: C 89.90; H 9.36. Calc. for $C_{13}H_{16}$: C 90.64; H 9.36).

1-Benzylindene V. (Method C).[7] 0.5 mole of indenyl magnesium bromide [19] in 250 ml of dry ether were reacted with 63.3 g (0.5 mole) of benzyl chloride in 100 ml of dry ether. Working up the resulting mixture afforded 1-benzylindene (39.1 g, 38 % calculated on indene), b.p. 114–115° (0.3 mm), n_D^{20} = 1.6035; lit.[7] value: b.p. 173–175° (12 mm).

Rearrangement of 1-benzylindene to 3-benzylindene. 1-Benzylindene isomerized to 3-benzylindene in a pyridine solution (2 M) containing 0.214 M of TEA. The procedure was followed by the NMR-technique and the rate constant determined, $k = 4.6 \times 10^{-4}$ sec^{-1} (30°).

1-Methylindene VI. (Method D).[13] 14.6 g (0.1 mole) of 3-methyl-1-indanone [20] (b.p. 114–116°, 10 mm) was reduced with 1.2 g of lithium aluminium hydride in 200 ml of dry ether. 1-Hydroxy-3-methylindane (12.7 g, 86 %) was obtained as white crystals, m.p. 73–74° (from petroleum ether); lit:[13] m.p. 69°. The alcohol was dehydrated by distillation over potassium bisulphate yielding 1-methylindene (7.4 g, 66 %), b.p. 63–65° (8.5 mm), n_D^{25} = 1.5558; lit.[13] values: b.p. 82° (15 mm), n_D^{20} = 1.5569.

Rearrangement of 1-methylindene. As previously reported,[1] 1-methylindene rearranges to 3-methylindene in a basic medium. TEA was used as catalyst. The pseudo-first order rate constant was calculated to be 3.0×10^{-4} sec^{-1} and 1.5×10^{-4} sec^{-1}, the concentration of catalyst being 0.257 and 0.129 M, respectively (30°).

1-Methyl-3-isopropylindene IX. Isopropyl magnesium bromide was prepared from 15.1 g (0.12 mole) of isopropyl bromide and 3.0 g (0.12 g atoms) of magnesium and to its solution in 100 ml of dry ether 14.7 g (0.10 mole) of 3-methyl-1-indanone were added dropwise under nitrogen. After complete addition the mixture was kept at gentle reflux for 15 h. 30 ml of a saturated ammonium chloride solution were added at 0°. The ether layer was separated, the water layer extracted with ether and the combined organic layers were washed and dried. Evaporation of the solvents yielded a thick oil, which in IR showed both hydroxyl and carbonyl absorption. Without further purification, the oil was dissolved in 70 ml of dry benzene and heated with 15 g of phosphorus pentoxide. At reflux temperature additional 5 g of the oxide were added. The mixture was kept at reflux for 10 min. The cooled benzene solution was washed with water and dried. Evaporation of the solvent gave 12.5 g of a yellow oil which was distilled in vacuum. The main fraction (7.5 g, 44 %) boiled at 51–54° (0.15 mm). NMR and IR analyses showed contamination with 3-methyl-1-indanone (about 5 %) and 1-methyl-3-isopropylideneindane (10–15 %). For further purification 1.0 g of the distilled product was chromatographed on 50 g silicic acid (Mallinckrodt). Elution with petroleum ether (b.p. 60–75°) afforded in the first fractions, pure 1-methyl-3-isopropylindene (200 mg), n_D^{20} = 1.5375,while the subsequent fractions also contained some 1-methyl-3-isopropylideneindane. (Found: C 90.46; H 9.48. Calc. for $C_{13}H_{16}$: C 90.63; H 9.37).

Rearrangement of 1-methyl-3-isopropylindene. For isolation of the pure equilibrium mixture 3.6 g of 1-methyl-3-isopropylindene were dissolved in 10 ml of pyridine and heated at 60° for 10 min with 1 ml of "Triton B" in pyridine. The pyridine was evaporated, the residue dissolved in ether, washed with diluted acetic acid, water, sodium bicarbonate solution, water, and dried. Evaporation of the solvent and distillation afforded 2.1 g, b.p. 101–105° (9 mm) of the two isomers: 3-methyl-1-isopropylindene, 80 %, and 1-methyl-3-isopropylindene, 20 %; the compositions were determined by NMR-spectroscopy.

1-Methyl-3-tert-butylindene VII. By the same method as described for 1-methyl-3-isopropylindene above, 1-methyl-3-*tert*-butylindene was prepared from 0.2 mole of *tert*-butyl magnesium chloride in dry benzene and 14.6 g (0.1 mole) of 3-methyl-1-indanone. On distillation no sharp boiling point was observed, due to the large amount of unreacted

ketone still present. 2.5 g of the main fraction (4.0 g, b.p. 100—112°, 9 mm) were chromatographed on 120 g of silicic acid (Mallinckrodt) yielding 0.75 g of the pure 1-methyl-3-tert-butylindene $n_D^{22} = 1.5327$, on elution with petroleum ether, (b.p. 60—75°). (Found: C 90.09; H 9.77. Calc. for $C_{14}H_{18}$: C 90.25; H 9.75).

*1-*tert*-Butyl-3-methylindene (VIII) from 1-methyl-3-*tert*-butylindene VII.* 280 mg of 1-methyl-3-*tert*-butylindene were dissolved in pyridine; butylamine was added to give a concentration of 0.70 M. The rearrangement proceeded to complete conversion to 1-*tert*-butyl-3-methylindene. The pseudo-first order rate constant at 30° was 3.6×10^{-5} sec^{-1}. The pyridine solution was evaporated and the residue chromatographed on 30 g of silicic acid (Mallinckrodt). Elution with petroleum ether (b.p. 60—75°) gave the pure 1-*tert*-butyl-3-methylindene, identified by the NMR-spectrum.

The preparation of the optically active substances mentioned in this paper, will be reported later.

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