297,* 295* (0.1, 0.1), 240,* 238* (10, 10), 225,* 223* (3, 3), 193, 191 (8, 8), 168 (17), 159* (7), 111* (100), 97* (5), 95* (4), 93* (9), 85 (25), 83 (18), 69 (8), 57 (38); ir (carbon tetrachloride) 2960 (s), 1665 (m), 1490 (w), 1480 (w), 1380 (w), 1272 (m), 1245 (s), 1065 (m), 860 (vs), 690 (m), 610 (w), 550 cm^{-1} (m). The ^1H and ^{31}P nmr spectral data for **3** are described in the text.

Acknowledgment. We appreciate the constructive criticisms offered by one of the referees. E. R. K. has been an NSF Trainee, 1970-present. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

Registry No.—**1,** 20859-13-6; **3,** 51270-67-8; **5,** 51270-68-9; HBr, 10035-10-6; PTB, 7789-60-8.

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(8) Part of this absorption overlapped with peaks due to **5.** Locations of such lines were initially inferred from anomalous intensities.

(9) See, for example, J. B. Conant and A. A. Cook, *J. Amer. Chem. Soc.*, **42,** 830 (1920).

(10) W. Rundel, *Chem. Ber.*, **102**, 374 (1964); mp after sublimation (40°, 15 mm) 43–44°.

(11) $[M + H]^+$ peaks three times as intense as the parent ions were observed at *m/e* 249 and 251.

(12) Any variation in conditions (*e.g.*, omission of argon, more concentrated or moist solutions, etc.) which permits the buildup of HBr provided product mixtures richer in **5**, sometimes to the virtual exclusion of **3.** Another fascinating feature of this reaction, as well as those described earlier,[1] is the inability to suppress the hydrolysis of (presumed intermediate) **2** to **3.** Even under strictly anhydrous conditions without aqueous work-up, **3** was the sole heterocyclic product observed.

(13) Compounds **3** and **5** are similar enough in volatility that sublimation (0.60 mm and 40°) provides a mixture only slightly enriched in **5** (up to 65% from 50%). Nor were any chromatographic techniques, including tlc, elution, or glc, found that would allow **3** to survive.

(14) Although we have not been able to directly substantiate this by mass balance, it seems that, during the purification of **3,** the amount of **5** recovered at each stage exceeds the decrease of **5** observed in the oil. This would support the assertion that **3** can decompose to **5,** *via* an intermediate similar to **4.**

(15) Asterisks mark the peaks common to derivatives of the isomeric ring system shown in reaction 1. The appearance of weak $[M + H]^+$ ions, rather than M^+, seems to be a characteristic of these systems.[1] A single peak at *m/e* 281 (4), overlapping the $[M - CH_3]$ doublet, suggests the presence of a higher molecular weight impurity.

A General Indene Synthesis *via* Cyclization of Phenyl-Substituted Allylic Cations

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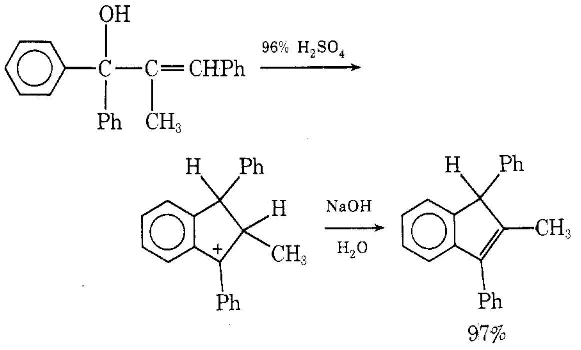
Received January 23, 1974

Indenes have been prepared by a number of cyclialkylation procedures, such as dehydration of phenyl-substituted diols and reaction of phenyl-substituted alkenes with phosphorus halides.[1-3] Recently, the reaction of *gem*-dihalocyclopropanes with benzene and aluminum chloride was used.[4] These procedures are of limited scope; so indenes have generally been prepared by treating Grignard or lithium reagents with an appropriate indanone followed by dehydration of the resulting indanol. The required indanones have usually been prepared by cyclization of β-phenyl-substituted carboxylic acids resulting from Reformatsky, Perkin, or Friedel–Crafts routes.[5,6] Overall, these routes consist of several steps with low overall yields and only moderate flexibility for the preparation of substituted derivatives.

Recently, we reported the generation of indanyl cations by dissolving phenyl-substituted allylic alcohols, of wide variety, into strongly acidic media (*i.e.*, FSO_3H, H_2SO_4, etc.).[7] Initially, acyclic allylic cations are formed. These then cyclize to give indanyl cations in the acidic media.[7] We have found that solutions of indanyl cations give good yields of the corresponding indenes when quenched into excess aqueous base. This fact, and the ease with which a variety of phenyl-substituted allylic alcohols can be prepared, make this indene synthesis a general and efficient procedure. A typical example is the cyclization of 1,1,3-triphenyl-2-methylpropenol to 1,3-diphenyl-2-methylindene in high yield (eq 1).



(1)

This method has several advantages over techniques employed previously. First, the overall yields are improved. Second, desired substitution at carbons 1, 2, and 3 is easily achieved in a few steps. For example, phenyl-substituted allylic alcohols in wide variety can be conveniently prepared by aldol condensation followed by treatment of the resulting α,β-unsaturated ketone with Grignard or lithium reagents. Alternatively, reaction of vinyl Grignard reagents with appropriate aldehydes or ketones give allylic alcohol precursors. These routes are outlined in Scheme I.

Scheme I

$$\begin{tikzcd} R_5R_4C{=}CR_3Li(MgX) + \dot{R}_2COR_1 \arrow[r] & R_5R_4C{=}CR_3C(OH)R_2R_1 \\ R_5COR_4 + R_3CH_2COR_2 \arrow[r, "\text{base}"'] & R_5R_4C{=}C(R_3)COR_2 \arrow[u, "\text{hydride reduction}", "\text{or } R_1Li(MgX)"'] \end{tikzcd}$$

Another advantage of this method is that the indanyl cations can be directly observed by nmr spectroscopy, allowing one to monitor the cyclization. Also, some indanyl cations further rearrange in solution when the temperature is raised.[8] This allows two possible indenes to be generated from the same precursor alcohol simply by choosing the temperature the acid solution is permitted to reach before quenching (for examples see Scheme II).

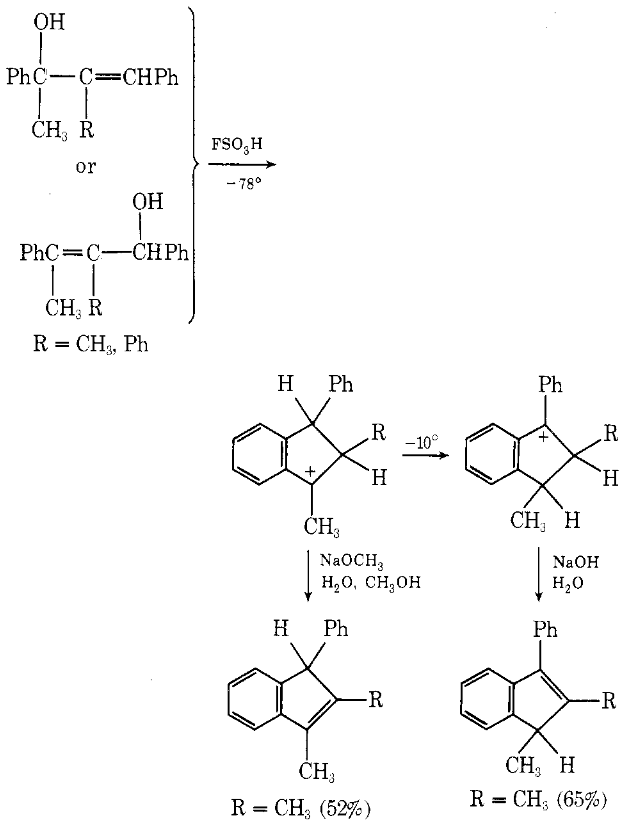
A few cases of indenes prepared by allylic cyclodehydration, presumably *via* transient indanyl cation intermediates, have appeared.[9,10] Bergman obtained an unspecified amount of 1,2-diphenylindene on treatment of 1,2,3-triphenylpropenol with dilute sulfuric acid followed by distillation.[9] Similarly, Koelsch converted 1,1,2,3,3-penta-

Table I
Synthesis of Indenes from Phenyl-Substituted Allylic Alcohols

Allylic alcohol	Registry no.	Indene product	Registry no.	Yield, %[a]
3-Methyl-2-phenyl-3-penten-2-ol	41231-83-8	1,2,3-Trimethylindene	4773-83-5	69
3,4-Dimethyl-2-phenyl-3-penten-2-ol	41231-84-9	1,2,3,3-Tetramethylindene	4705-87-7	58 (71)
2,4-Diphenyl-3-buten-2-ol	41231-78-1	1-Phenyl-3-methylindene	22360-62-9	72 (87)
2,3-Diphenyl-4-methyl-3-penten-2-ol	41231-85-0	2-Phenyl-1,3,3-trimethylindene	51310-24-8	74 (84)
1,1,3-Triphenyl-2-propenol	4663-36-9	1,3-Diphenylindene	4467-88-3	84
2,3,4-Triphenyl-3-buten-2-ol	41231-81-6	1,2-Diphenyl-3-methylindene	51310-25-9	84
2-Methyl-1,1,3-triphenyl-2-propenol	41231-87-2	1,3-Diphenyl-2-methylindene	51310-26-0	97

[a] Yields are given for reactions employing 96% H_2SO_4 with the exception that those in parentheses resulted from the use of 90% H_2SO_4.

Scheme II



phenylpropenol to 1,2,3,3-tetraphenylindene, also in unspecified yields.[10] Our procedure differs in that excess strong acid is used as the solvent. This medium effects nearly quantitative cyclodehydration of the alcohol (*via* the acyclic allylic cation) to a stable indanyl cation. By carefully quenching the cation solution into excess base by rapid dispersal techniques, second-order alkylation reactions, which prevail in less acid media,[11] are avoided. Generally, 90% H_2SO_4 gave better yields than 96% H_2SO_4. This is probably due both to the lowered sulfonating power of 90% H_2SO_4[12] and to its lower viscosity, which permits rapid stirring and dissolving of the alcohol without hot spots developing. Table I summarizes the synthetic results.

Experimental Section

Preparation of Phenyl-Substituted Allylic Alcohols. The syntheses of all alcohols listed in Scheme I or Table I were reported previously.[7]

Conversion of Allylic Alcohols to Indenes. All indenes in Table I were prepared as follows. One gram of phenyl-substituted allylic alcohol was dissolved in a few milliliters of carbon tetrachloride, the actual volume depending on the solubility of a given alcohol in carbon tetrachloride. These solutions were then added dropwise to 3 ml of 96% (or 90%) sulfuric acid at 0-5° with rapid stirring. When addition was complete stirring was stopped and the acid layer was allowed to settle to the bottom. The acid layer was removed and slowly added to an excess of cold, dilute (5-15%) sodium hydroxide. The residual base was then neutralized with 1:1 hydrochloric acid-water. The neutralized mixture was extracted twice with ether. The extract was dried (anhydrous sodium carbonate) and evaporated, and the residue was recrystallized or distilled, as necessary. Alternatively, the allylic alcohol was dissolved in SO_2 at −78° and this solution was added dropwise to FSO_3H at −78° with rapid stirring. The acid was warmed to the desired temperature and quenched.

1,2,3-Trimethylindene: bp 97-100° (10 mm) [lit.[13] bp 100-103° (11 mm)]; nmr (CCl_4) τ 8.89 (d, 3 H, J = 7.5 Hz, CH_3 at C-1), 8.20 (s, 3 H, CH_3 at C-2), 8.13 (s, 3 H, CH_3 at C-3), 7.07 (q, 1 H, J = 7.5 Hz, C-1 H), and 2.99 (m, 4 H, phenyl C-H).

1,2,3,3-Tetramethylindene: bp 47° (0.23 mm) [lit.[14] bp 113° (17 mm)]; nmr (CCl_4) τ 8.90 (s, 6 H, methyls at C-3), 8.24 (s, 3 H, CH_3 at C-2), 8.10 (s, 3 H, CH_3 at C-1), and 2.99 (m, 4 H, phenyl C-H).

1-Phenyl-3-methylindene: bp 116° (0.88 mm) [lit.[15] bp 87° (0.01 mm)]; nmr (CCl_4) τ 8.81 (d, 3 H, J = 7.5 Hz, CH_3 at C-3), 6.65 (q, 1 H, J = 7.5 Hz with additional 2-Hz coupling to C-2 H, C-1 H), 3.73 (d, 1 H, J = 2.0 Hz, C-2 H), and 2.74 (m, 9 H, phenyl C-H).

2-Phenyl-1,3,3-trimethylindene (recrystallized from EtOH): mp 82°; nmr (CCl_4) τ 8.69 (s, 6 H, CH_3 groups at C-3), 8.05 (s, 3 H, CH_3 at C-1), and 2.79 (m, 9 H, phenyl C-H). *Anal.* Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.08; H, 7.85.

1,3-Diphenylindene (recrystallized from glacial acetic acid): mp 66-67° (lit.[16] mp 68-69°) and mp 84-85° when recrystallized from EtOH (lit.[16] mp 84-85°); nmr (CCl_4) τ 5.45 (d, 1 H, J = 2.0 Hz, C-1 H), 3.51 (d, 1 H, J = 2.0 Hz, C-2 H), and 2.66 (m, 14 H, phenyl C-H).

1,2-Diphenyl-3-methylindene (recrystallized from EtOH): mp 92-93°; nmr (CCl_4) τ 7.75 (d, 3 H, J = 2.0 Hz, CH_3 at C-3), 5.24 (q, 1 H, J = 2.0 Hz, C-3 H), and 2.97 (m, 14 H, phenyl C-H). *Anal.* Calcd for $C_{22}H_{18}$: C, 93.57; H, 6.43. Found: C, 93.70; H, 6.17.

1,3-Diphenyl-2-methylindene (recrystallized from EtOH): mp 109-110.5° (lit.[17] mp 108°); nmr (CCl_4) τ 8.14 (s, 3 H, CH_3 at C-2), 5.71 (s, 1 H, C-1 H), and 2.76 (m, 14 H, phenyl C-H).

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