fully augmented with 9-propylfluorene. The minor peak constituted 17.2% of the total chromatogram and was successfully augmented with 9-isopropylfluorene.

Registry No.—5, 27971-70-6; methyl 2,2-biphenylenecyclopropanecarboxylate, 27921-38-6; 2,2-biphenylenecyclopropylcarbinol, 27921-39-7.

New Friedel–Crafts Chemistry. XXIV.[1] On the Mechanism of Cyclidehydration of Primary Phenylalkanols to Indans[2]

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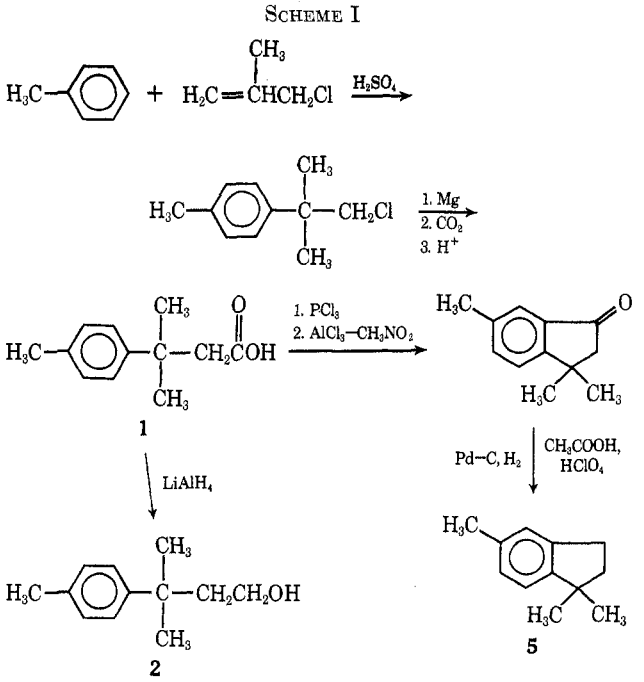
The mechanism of acid-catalyzed cyclidehydration of primary alcohols to five-membered ring compounds was explored by determining the products obtained by subjecting 3-methyl-3-(*p*-tolyl)-1-butanol (**2**) to acid-catalyzed dehydration. These products were found to be a mixture of the expected open-chain rearranged products, 2-methyl-3-(*p*-tolyl)-2-butene (**21**) and 2-methyl-3-(*p*-tolyl)butane (**22**), together with rearranged and nonrearranged cyclidehydration products. The cyclized compounds (*ca.* 55% of the total product) were a mixture of 1,1,4-, 1,1,5-, 1,1,6-, and 1,1,7-trimethylindan isomers in a ratio of 55:17:23:5, respectively. A mechanism invoking anchimerically assisted ionization through Ar_1-4 and Ar_2-5 participations in combination with the usual Wagner–Meerwein type shifts is suggested to account for the cyclized products. On the basis of product composition, the overall ratio of Ar_1-4 to Ar_2-5 participation may be at least 3.5 to 1.

In a previous paper of this series[1] we reported among other things that the treatment of 3-methyl-3-phenyl-1-butanol with phosphoric acid at 230° resulted in some cyclization to 1,1-dimethylindan. On the other hand, similar treatment of 3-phenyl-1-propanol with phosphoric acid produced no detectable amounts of the expected cyclic product, indan. To account for the role of the *gem*-methyls in the above compound, as well as for the role of the keto group in α-alkyl-β-hydroxypropiophenones in promoting ring closure of such primary alcohols to five-membered ring products, we proposed a mechanism[4] involving Ar_1-4 participation and 1,3-phenyl migration to yield intermediates capable of cyclizing to five-membered ring compounds. However, at the time we suggested our mechanism, there were no available experimental data to support it or to distinguish it from a similar likely mechanism that involves Ar_2-5 rather than Ar_1-4 type participation.

The present work was designed to determine the nature and the extent of contribution of the various intermediates responsible for the cyclization of such primary alcohols to five-membered ring compounds by subjecting the methyl-labeled derivative, 3-methyl-3-(*p*-tolyl)-1-butanol (**2**), to the same cyclization conditions and by studying the cyclized products obtained.

Synthesis of Starting Material and Products.—Since a number of isomeric trimethylindans were expected to result from the phosphoric acid induced cyclization of 3-methyl-3-(*p*-tolyl)-1-butanol (**2**), we developed methods to obtain them separately. Unequivocal syntheses of some of the materials needed are outlined in Schemes I and II. Scheme I describes the synthesis of the starting alcohol **2** and 1,1,5-trimethylindan (**5**) from the acid precursor **1**. Scheme II outlines the general steps used for the synthesis of the three isomeric trimethylindans, **4**, **6**, and **7**. Starting with *o*-tolualdehyde (**3**, R = *o*-CH_3), *p*-tolualdehyde (**3**, R = *p*-CH_3), and *m*-tolualdehyde (**3**, R = *m*-CH_3), this procedure gave 1,1,4-trimethylindan (**4**), 1,1,6-trimethylindan (**6**), and a mixture of 1,1,5-trimethylindan (**5**) and 1,1,7-trimethylindan (**7**), respectively. The components of the latter mixture were separated by preparative gas chromatography.

SCHEME I



Results and Discussion

The treatment of 3-methyl-3-(*p*-tolyl)-1-butanol (**2**) with phosphoric acid was carried out under conditions similar to those applied previously for 3-methyl-3-phenyl-1-butanol.[1,4–6] The products of this treatment were analyzed before and after subjection to catalytic hydrogenation and the results of this analysis are given in Table I.

(1) Part XIX: A. A. Khalaf and R. M. Roberts, *J. Org. Chem.*, **34**, 3571 (1969).

(2) Generous support of this research, including a postdoctoral fellowship for A. A. Khalaf, by the Robert A. Welch Foundation, is gratefully acknowledged.

(3) On leave of absence from the Chemistry Department, Assiut University, Assiut, U. A. R.

(4) See Schemes I and II of ref 1.

(5) M. T. Bogert and D. Davidson, *J. Amer. Chem. Soc.*, **56**, 185 (1934).

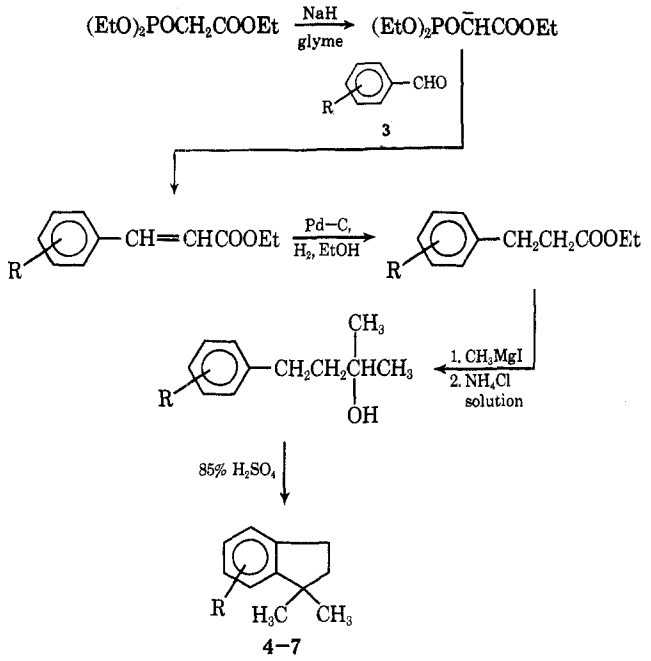
(6) R. O. Roblin, Jr., D. Davidson, and M. T. Bogert, *ibid.*, **57**, 151 (1935).

TABLE I

TREATMENT OF 3-METHYL-3-(*p*-TOLYL)-1-BUTANOL WITH PHOSPHORIC ACID. MONOMERIC PRODUCTS BEFORE AND AFTER CATALYTIC HYDROGENATION

	p-tert-Pentyltoluene (19)	2-Methyl-3-(*p*-tolyl)-butane (22)	2-Methyl-3-(*p*-tolyl)-2-butene (21)	Trimethylindans 1,1,6- (6)	1,1,4- (4)	1,1,5- (5)	1,1,7- (7)	Unidentified
Products before hydrogenation	Trace	6	46		31	10	3	4
Products after hydrogenation	Trace	40		13	32	10	3	2
Normalized per cent of cyclized products				22.4	55.2	17.2	5.2	

SCHEME II



3, R = *o*-CH_3 ⟶ 1,1,4-trimethylindan (4)

3, R = *p*-CH_3 ⟶ 1,1,6-trimethylindan (6)

3, R = *m*-CH_3 ⟶ a mixture of 1,1,5-trimethylindan (5) and 1,1,7-trimethylindan (7)

With reference to the data in Table I it is clear that, as in the case of 3-methyl-3-phenyl-1-butanol, both cyclidehydration and rearranged normal dehydration products were formed. However, it should be noted that in the present case the cyclidehydration products comprised about 55% of the total monomeric mixture. This value should be contrasted with 18% in the case of 3-methyl-3-phenyl-1-propanol.

With respect to the mechanism of dehydration of alcohol 2, it is convenient at this point to consider two possible paths, one for cyclidehydration and the other for normal dehydration. It will be evident in the following discussion whether or not these two paths are related to each other and to what extent.

Turning now to the cyclidehydration path, it is important to point out that any suggested path should offer reasonable explanations for the following observations: (1) the effect of the ring methyl group in enhancing the cyclization of 3-methyl-3-(*p*-tolyl)-1-butanol (2) relative to 3-methyl-3-phenyl-1-butanol, and the failure of 3-phenyl-1-butanol to cyclize at all; (2) the production of the rearranged trimethylindans 4, 6, and 7 from the cyclidehydration of 2; and (3) the necessary presence in the alkanol chain of a carbon directly attached to the aromatic ring and capable of stabilizing a positive charge, as in a dimethylated or ketonized carbon atom.

The above observations can be accounted for in terms of one or more of the following postulated reaction paths.

(1) An intermolecular dealkylation–realkylation mechanism in which the alkanol side chain is displaced by a proton in the initial step to yield an aromatic hydrocarbon and a tertiary carbonium ion. Realkylation may then occur at the ortho and meta positions, followed by cyclidehydration. A similar mechanism was previously invoked by Barclay[7] to explain the analogous cyclization of α-alkyl-β-hydroxypropiophenones.

(2) A direct intramolecular cyclization mechanism with or without Ar_2-5 participation, followed by methyl reorientations. (The formation of only 1,1,5-trimethylindan can be rationalized without invoking the methyl reorientations.)

(3) An anchimerically assisted ionization mechanism in which various types of aryl participation and migration operate in such a way as to produce the observed rearranged indans. An outline of such combined processes is given in Scheme III.

Examination of the above mechanisms in the light of the available experimental data leads to the following decisions about their credibility.

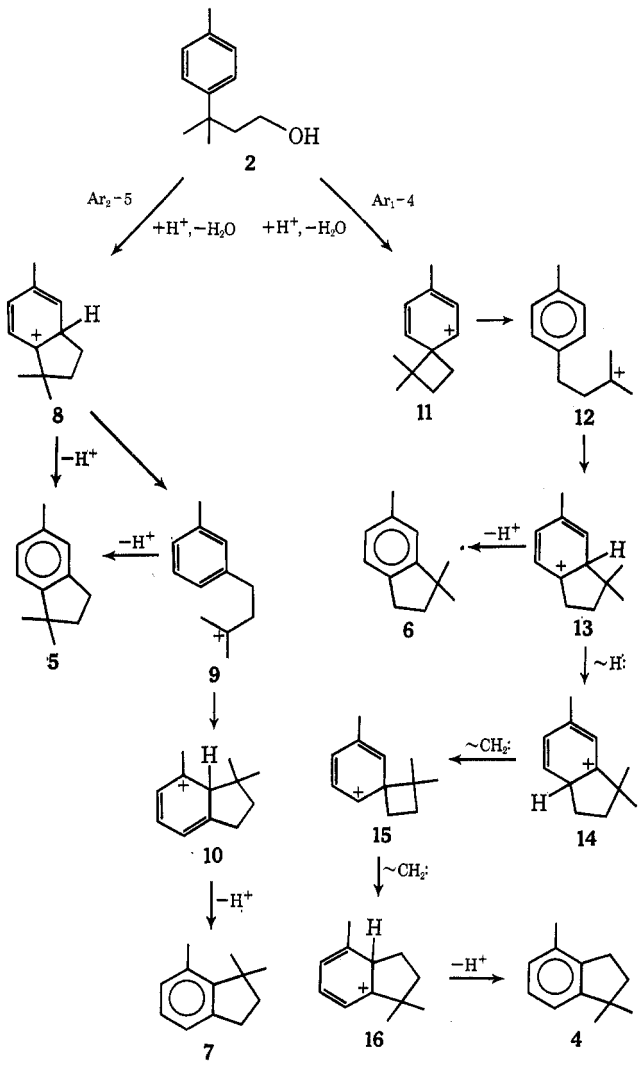
Path 1 can be excluded on the basis of crossover experiments in which 3-methyl-3-(*p*-tolyl)-1-butanol and 3-methyl-3-phenyl-1-butanol were subjected to the cyclization conditions in the presence of benzene and toluene, respectively. In these experiments none of the crossed cyclization products expected from such an intermolecular alkylation–dealkylation mechanism were detected.

The second mechanism was also abandoned on the ground that the methyl reorientations involved do not occur under the cyclization conditions, as shown by the following experiments. Treatment of all four of the isomeric trimethylindans 4, 5, 6, and 7 with phosphoric acid under conditions duplicating those used for cyclization resulted in no methyl reorientation; the hydrocarbons were recovered unchanged.

On the basis of the above results, we are left with the anchimerically assisted ionization pathways postulated in Scheme III as the only alternative that can satisfactorily account for the results. Besides explaining the formation of rearranged trimethylindans, this mechanism also rationalizes the observed enhanced cy-

(7) L. R. C. Barclay in "Friedel-Crafts and Related Reactions," Vol. II, G. A. Olah, Ed., Interscience, New York, N. Y., 1964, p 826.

SCHEME III



clization of **2**, relative to 3-methyl-3-phenyl-1-butanol, in terms of the established higher participating ability of the tolyl group as compared to the phenyl group.

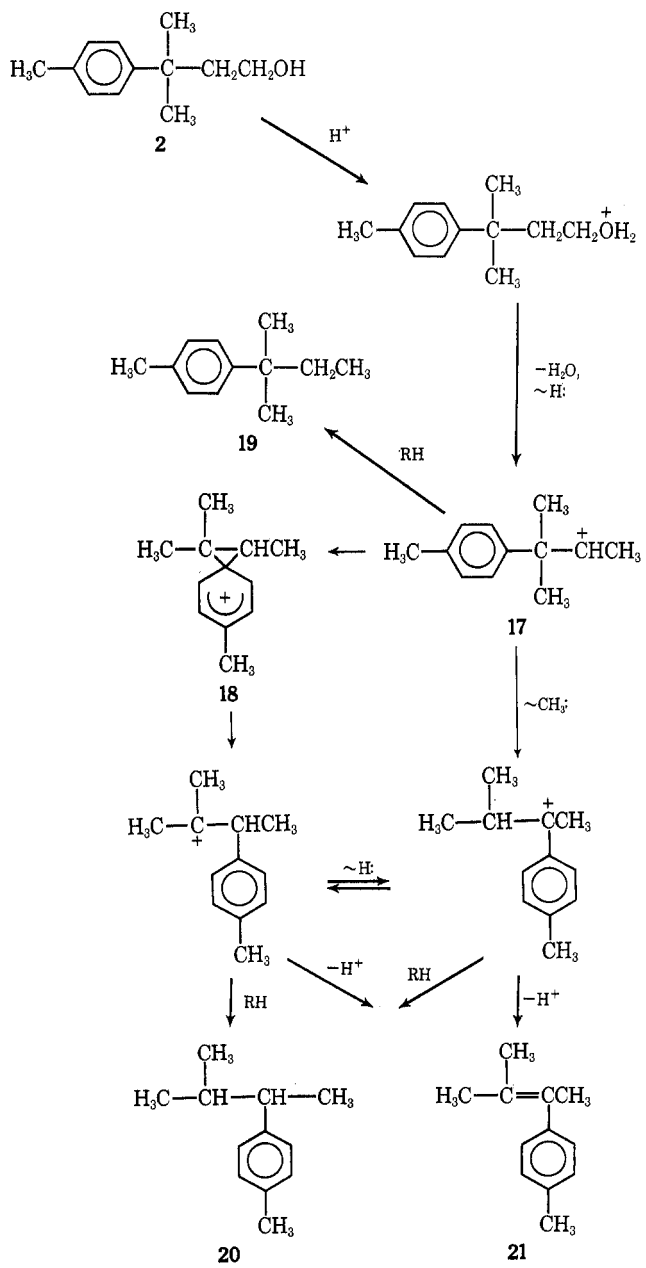
In Scheme III we show the formation of **8** by Ar_2-5 participation, followed by direct deprotonation to give **5**. 1,1,7-Trimethylindan (**7**) is produced from **8** by ring opening to give the tertiary carbonium ion **9**, followed by a recyclization ortho to the ring methyl group. Although some **5** may arise *via* **9** as an intermediate, the direct deprotonation of **8** must represent the major route for its production, because a higher proportion of **5** to **7** is obtained from **2** than in the case of cyclidehydration of 2-methyl-4-(*m*-tolyl)-2-butanol with either sulfuric or phosphoric acid, a reaction which should involve the ion **9** as a common intermediate for the formation of **5** and **7**.

1,1,6-Trimethylindan (**6**) was produced in an amount about equal to the sum of the amounts of **5** and **7**. Its formation is shown as involving Ar_1-4 participation to produce **11**, followed by ring opening to give the tertiary carbonium ion **12**, which then can cyclize to give **13** and **6**.

The finding of 1,1,4-trimethylindan (**4**) as the major trimethylindan isomer was surprising, and we have no completely satisfactory explanation for it. One possible pathway for its formation is outlined in Scheme III. According to this rationale, as an alternative to losing a proton to yield **6**, intermediate **13** may undergo hydride and methylene shifts to rearrange to **16** which then yields **4**. The intermediate ions **14** and **16** should be stabilized by the electron release of the ring methyl group, and this may provide a driving force for the rearrangements.

We have so far been concerned with mechanisms for the formation of the isomeric trimethylindans produced by cyclidehydration of **2**, but no attention has been given to the source of the noncyclized products **19**, **21**, and **22** (see Table I). These must arise from the initial formation of the carbonium ion **17**, or its equivalent complex, followed by the usual rearrangements, hydride exchanges, and proton losses, as outlined in Scheme IV. Although some participation by the *p*-

SCHEME IV



tolyl group may be involved in the formation of the noncyclized products, as indicated by the phenonium ion **18** as a possible intermediate, this must occur in a step subsequent to the loss of water. Thus it seems

unlikely that any participation involved in the formation of the rearranged noncyclized products is competitive with the Ar_1-4 and Ar_2-5 participations as a product-determining step.

The cyclidehydration products from **2** comprise about 60% of the total products observed, and the noncyclized products comprise about 40% (on the basis of analysis of the product mixture after hydrogenation; *cf.* Table I). From the proportions of the isomeric trimethylindans found, an estimate can be made of the relative importance of Ar_1-4 and Ar_2-5 participation. On the basis of the mechanisms proposed in Scheme III, the approximately equal amounts of **6** and of **5** + **7** observed imply that the cyclidehydrations proceed through Ar_1-4 participation at least to the same extent as through Ar_2-5. If the mechanism of formation of **4** is as proposed, since it involves an initial Ar_1-4 participation, the overall ratio of Ar_1-4 to Ar_2-5 participation would be at least 3.5 to 1.[8]

Experimental Section[9]

The purity (unless specified, 95% or higher) and identity of the starting material and of the final products were determined by glpc, ir, and nmr analysis and, in some cases, also by mass spectrometric analysis; except where otherwise specified, yields in each step were not less than 70%.

Synthesis of Starting Carbinols.—3-Methyl-3-phenyl-1-butanol was prepared as previously described.[1] **3-Methyl-3-(*p*-tolyl)-1-butanol** (**2**) was prepared as follows. Reaction of methallyl chloride and toluene in the presence of sulfuric acid,[10] following the procedure described for neophyl chloride,[11,12] gave 2-methyl-2-(*p*-tolyl)-1-chloropropane contaminated with *ca.* 7% of other isomers: bp 110–111° (6.5 mm), n^{24}D 1.5224 [lit.[10] bp 110.5–112.5° (10 mm)]; nmr δ 7.27–6.87 (m, A^2B^2 pattern with strong doublet centered at 7.07, 4, aromatic), 3.45 (s, 2, CH_2Cl), 2.23 (s, 3, $ArCH_3$), and 1.3 ppm (s, 6, *gem*-methyls). The chloride was treated with magnesium in dry ether and the resulting Grignard reagent was carbonated (Dry Ice) to give β-(*p*-tolyl)isovaleric acid (**1**): mp 75–76° (lit.[13] mp 77°); nmr δ 11.5 (s, 1, COOH), 7.31–6.90 (m, A^2B^2 with strong doublet centered at 7.1, 4, aromatic), 2.55 (s, 2, CH_2CO), 2.3 (s, 3, $ArCH_3$), and 1.43 ppm (s, 6, *gem*-methyls).

Reduction of the acid with $LiAlH_4$ in dry ether gave 3-methyl-3-(*p*-tolyl)-1-butanol (**2**): bp 95–96° (0.45 mm), n^{26}D 1.5166 [lit.[2] bp 141–142° (11 mm)]; nmr δ 7.25–6.87 (m, A^2B^2 with strong doublet centered at 7.07, 4, aromatic), 3.60 (s, 1, OH), 3.30 (t, 2, J = 7 Hz, CH_2O), 2.25 (s, 3, $ArCH_3$), 1.77 (t, 2, J = 7 Hz, CH_2), and 1.23 ppm (s, 6, *gem*-methyls).

Synthesis of Authentic Hydrocarbons.—Of the required hydrocarbons, *p-tert*-pentyltoluene (**19**)[14] and 2-methyl-3-(*p*-tolyl)butane (**22**)[15] were available from previous work. The unequivocal methods applied for the synthesis of other required hydrocarbons are outlined below.

3-Methyl-1-*p*-tolylbutane.—*p*-Tolualdehyde was treated with isobutylmagnesium chloride in dry ether to give isobutyl-(*p*-tolyl)carbinol. Reduction by hydrogen and palladium on carbon in glacial acetic acid containing a little perchloric acid[16] gave the title compound: bp 132–133° (80 mm) (lit.[17] bp 213°); n^{25}D 1.4822; nmr δ 6.93 (s, 4, aromatic), 2.52 (t, 2, J = 7 Hz, $ArCH_2$), 2.23 (s, 3, $ArCH_3$), 1.80–1.20 (an apparent triplet with J = 7 Hz superimposed on a weak multiplet, 3, $CH_2CH<$), and 0.92 ppm (d, 6, J = 5.5 Hz, *gem*-methyls). The title compound was not present in the reaction mixture from the treatment of **2** with phosphoric acid.

1,1,5-Trimethylindan (**5**).—Reaction of β-(*p*-tolyl)isovaleric acid (**1**) and phosphorus trichloride gave β-(*p*-tolyl)isovaleryl chloride.[18a] Ring closure by $AlCl_3$–CH_3NO_2 in CS_2[18a] yielded 3,3,6-trimethyl-1-indanone: bp 73–74° (0.15 mm) [lit.[18a] bp 110° (3.8 mm)]; n^{26}D 1.5367; nmr δ 7.33 (s, 3, aromatic), 2.45 (s, 2, CH_2CO), 2.33 (s, 3, $ArCH_3$), and 1.34 ppm (s, 6, *gem*-methyls). The indanone was reduced by hydrogen and palladium on carbon in glacial acetic acid[16] to give 1,1,5-trimethylindan (**5**): bp 64° (3.7 mm), n^{26}D 1.5113 [lit.[18b] 87–87.5° (11 mm), n^{24}D 1.5111]; nmr δ 6.87 (s, 3, aromatic), 2.80 (t, 2, J = 7 Hz, benzylic CH_2), 2.27 (s, 3, $ArCH_3$), 1.85 (t, 2, J = 7 Hz, CH_2), and 1.20 ppm (s, 6, *gem*-methyls).

1,1,4-Trimethylindan (**4**).—Reaction of *o*-tolualdehyde with carbethoxymethylphosphonate anion, $(EtO)_2POCHCOOEt$, in dry 1,2-dimethoxyethane, following essentially the procedure given by Wadsworth and Emmons,[19] with the exception that the reflux period was extended to 1.5 hr, gave ethyl *o*-methylcinnamate: bp 118–119° (2.7 mm); n^{24}D 1.5520; nmr δ 7.89 (d, 1, J = 16 Hz, ArCH=), 7.59–7.00 (m, 4, aromatic), 6.23 (d, 1, J = 16 Hz, =CHCO), 4.13 (q, 2, J = 7 Hz, OCH_2), 2.37 (s, 3, $ArCH_3$), and 1.29 ppm (t, 3, J = 7 Hz, OCH_2CH_3). Reduction of the cinnamate ester using hydrogen and palladium on carbon in ethanol gave ethyl *o*-methylhydrocinnamate:[20] bp 108–109° (2.9 mm); n^{24}D 1.4975; nmr δ 7.00 (s, 4, aromatic), 4.07 (q, 2, J = 7 Hz, OCH_2), 3.70–2.30 (m, AA'BB' pattern almost symmetric about 2.67, 4, $ArCH_2CH_2CO$), 2.28 (s, 3, $ArCH_3$), and 1.17 ppm (t, 3, J = 7 Hz, CH_2CH_3). Reaction of the hydrocinnamate ester with methylmagnesium iodide and decomposition with saturated ammonium chloride solution gave 2-methyl-4-(*o*-tolyl)-2-butanol: bp 102° (1.9 mm); n^{24}D 1.5064; nmr δ 6.99 (s, 4, aromatic), 2.90 (s, 1, OH), 2.82–2.43 (m, low-field part of an AA'BB' system, 2, $ArCH_2CH_2$), 2.25 (s, 3, $ArCH_3$), 1.83–1.45 (m, high-field part of the AA'BB' system, 2, $ArCH_2CH_2$), and 1.23 ppm (s, 6, *gem*-methyls). Cyclidehydration of the above alcohol with 85% sulfuric acid[1] gave 1,1,4-trimethylindan (**4**) (40%): bp 67° (2.75 mm); n^{26}D 1.5142; nmr δ 7.13–6.67 (m, with strong doublet centered at 6.87, 3, aromatic), 2.27 (t, 2, J = 7 Hz, benzylic CH_2), 2.17 (s, 3, $ArCH_3$), 1.83 (t, 2, J = 7 Hz, CH_2), and 1.18 ppm (s, 6, *gem*-methyls); mass spectrum (70 eV) m/e 160 molecular ion.

Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.71; H, 10.14.

1,1,6-Trimethylindan (**6**).—Reaction of *p*-tolualdehyde with carbethoxymethylphosphonate anion in dry 1,2-dimethoxyethane[19] gave ethyl *p*-methylcinnamate: bp 180–181° (30 mm), n^{24}D 1.5505 [lit.[21] 158–159° (17 mm), $n^{15.9}$D 1.5630]; nmr δ 7.55 (d, 1, J = 16 Hz, ArCH=), 7.30 and 7.03 (two doublets, 4, J = 8 Hz, ortho and meta aromatic protons, respectively), 6.25 (d, 1, J = 16 Hz, =CHCO), 4.7 (q, 2, J = 7 Hz, OCH_2), 2.27 (s, 3, $ArCH_3$), and 1.25 ppm (t, 3, J = 7 Hz, CH_2CH_3). Hydrogenation of the ester using hydrogen and palladium on carbon in ethanol gave ethyl *p*-methylhydrocinnamate: bp 146–147° (34 mm) (lit.[22] 263–265°) n^{24}D 1.4935; nmr δ 6.98 (s, 4, aromatic), 4.39 (q, 2, J = 7 Hz, OCH_2), 3.07–2.33 (complex AA'BB' multiplet almost symmetric about 270, 4, $ArCH_2CH_2$), 2.28 (s, 3, $ArCH_3$), and 1.15 ppm (t, 3, J = 7 Hz, CH_3). Reaction of the hydrocinnamate ester with methylmagnesium iodide

(8) Actually, intermediates **8** and **10** may also arise from rearrangements of **11** and **15**, respectively, a possibility which reduces still further the requirement of Ar_2-5 participation.

(9) Microanalysis was performed by Galbraith Laboratories, Inc., Knoxville, Tenn. The nmr spectra were determined in CCl_4 on a Varian A-60 instrument. A Beckman IR-5A spectrophotometer was used to record the ir spectra. The glpc analysis was carried out using a Varian Aerograph Hy-Fi Model 600-D instrument. The following columns were used: (1) a 50 ft × 0.125 in. silicone oil DC 550–Hypak column operated at 150–160° with nitrogen carrier gas at 60 psi; (2) a 16 ft × 0.125 in. DEGA (25%) column operated at 130–140° with nitrogen carrier gas at 22–25 psi; (3) a 10 ft × 0.125 in Apiezon L (20%) on Chromosorb W (30–60 mesh) column operated at 150–170° with nitrogen carrier gas at 7–9 psi.

(10) Yu. G. Mamedaliev, R. A. Babakhanov, and M. N. Magerramov, *Azerb. Khim. Zh.*, **6**, 37 (1961); *Chem. Abstr.*, **59**, 7398 (1963).

(11) W. T. Smith, Jr., and J. T. Sellas, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 702.

(12) A. A. Khalaf, Ph.D. Dissertation, The University of Texas, 1965.

(13) J. Colonge and L. Pichat, *Bull. Soc. Chim. Fr.*, 177 (1949).

(14) R. M. Roberts and S. E. McGuire, *J. Org. Chem.*, **35**, 102 (1970).

(15) A. A. Khalaf and R. M. Roberts, *ibid.*, **35**, 3717 (1970).

(16) R. M. Roberts, G. A. Ropp, and O. K. Neville, *J. Amer. Chem. Soc.*, **77**, 1764 (1955).

(17) S. V. Bigot and R. Fittig, *Justus Liebigs Ann. Chem.*, **141**, 162 (1967).

(18) (a) J. Colonge and G. Weinstein, *Bull. Soc. Chim. Fr.*, 961 (1951); (b) G. Buchi, K. Biemann, B. Vittimberga, and M. Stoll, *J. Amer. Chem. Soc.*, **78**, 2622 (1956).

(19) W. S. Wadsworth, Jr., and W. D. Emmons, *ibid.*, **83**, 1733 (1961).

(20) Characterized by hydrolysis to *o*-methylhydrocinnamic acid, mp 101–102°; Young [*Ber.*, **25**, 2104 (1892)] reported mp 102°.

(21) K. V. Auwers, *Ber.*, **45**, 2781 (1912).

(22) C. Willgerodt and W. Hambrecht, *J. Prakt. Chem.*, **81**, 77 (1910).

and decomposition with saturated ammonium chloride gave 2-methyl-4-(*p*-tolyl)-2-butanol: bp 113–114° (4.5 mm), mp 41–43° [lit.[23] bp 83.5–84.5° (0.4 mm), mp 42.5–43.1°]; nmr δ 6.97 (s, 4, aromatic), 2.80–2.45 (m, 2, $ArCH_2$), 2.99 (s, superimposed on latter multiplet, 1, OH), 2.27 (s, 3, $ArCH_3$), 1.87–1.50 (m, 2, $ArCH_2CH_2$), and 1.20 ppm [s, 6, *gem*-methyls]. Cyclidehydration of the tertiary alcohol with 85% sulfuric acid gave 1,1,6-trimethylindan (**6**) (50%): bp 88–90° (0.3 mm), $n^{26}D$ 1.5113 [lit.[23] bp 49.1–49.5° (1.1 mm), $n^{24}D$ 1.5133]; nmr δ 7.07–6.70 (m, 3, aromatic), 2.78 (t, 2, J = 7 Hz, $ArCH_2$), 2.27 (s, 3, $ArCH_3$), 1.85 (t, 2, J = 7 Hz, CH_2), and 1.20 ppm (s, 6, *gem*-methyls).

1,1,7-Trimethylindan (7).—Reaction of *m*-tolualdehyde with carbethoxymethylphosphonate anion in 1,2-dimethoxyethane[19] gave ethyl *m*-methylcinnamate:[24] bp 101–102° (2.0 mm); $n^{24}D$ 1.5505; nmr δ 7.57 (d, 1, J = 16 Hz, ArCH=), 7.37–7.00 (m, 4, aromatic), 6.33 (d, 1, J = 16 Hz, =CHCO), 4.22 (t, 2, J = 7 Hz, OCH_2), 2.31 (s, 3, $ArCH_3$), and 1.30 ppm (t, 3, J = 7 Hz, CH_3). Reduction of the ester with hydrogen and palladium on carbon in ethanol gave ethyl *m*-methylhydrocinnamate:[25] bp 117–118° (4.7 mm); $n^{24}D$ 1.4937; nmr δ 7.25–6.70 (m, 4, aromatic), 4.40 (q, 2, J = 7 Hz, OCH_2), 3.05–2.17 (complex AA'BB' multiplet, 4, $ArCH_2CH_2$), 2.27 (s, superimposed on the latter complex, 3, $ArCH_3$), and 1.17 ppm (t, 3, J = 7 Hz, CH_3). The hydrocinnamate ester was allowed to react with methylmagnesium iodide followed by decomposition with saturated ammonium chloride to give 2-methyl-4-(*m*-tolyl)-2-butanol: bp 88–89° (0.5 mm); $n^{24}D$ 1.5063; nmr δ 7.23–6.70 (weak multiplet at base with strong broadened singlet at 6.91, 4, aromatic), 2.93 (s, 1, OH), 2.80–2.30 (m, low-field part of AA'BB' system, 2, $ArCH_2CH_2$), 2.23 (s, 3, $ArCH_3$), 1.97–1.50 (m, high-field part of the AA'BB' system, 2, $ArCH_2CH_2$), and 1.20 ppm (s, 6, *gem*-methyls). Cyclidehydration of this alcohol with 85% sulfuric acid at room temperature gave 15% yield of a product, bp 82–89° (7.8 mm). This was shown to be composed of 1,1,5-trimethylindan (**5**) (68%) and 1,1,7-trimethylindan (**7**) (32%). Cyclidehydration of the same alcohol with phosphoric acid at 230° gave 50% yield of a product consisting of 1,1,5- and 1,1,7-trimethylindan in a per cent ratio of 53:47, respectively. These two components were separated by preparative glpc using an Aerograph Autoprep Model A-700 equipped with a 12 ft × 0.25 in. column[26] packed with cyanosilicone (30%) on 60–80 mesh Chromosorb at 140°. The 1,1,5-trimethylindan (**5**) obtained was identical in all respects with the same compound prepared previously, and the 1,1,7-trimethylindan (**7**, *ca.* 90% pure) had the following properties: $n^{26}D$ 1.5190; nmr δ 6.70–7.70 (m, with strong singlet at 6.87, 3, aromatic), 2.79 (t, 2, J = 7 Hz, benzylic CH_2), 2.33 (s, 3, $ArCH_3$), 1.85 (t, 2, J = 7 Hz, CH_2), and 1.32 ppm (s, 6, *gem*-methyls); mass spectrum (70 eV) *m/e* 160 molecular ion.

Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.80; H, 10.15.

Reactions of 3-Methyl-3-(*p*-tolyl)-1-butanol (2) with Phosphoric Acid.—The procedure described previously for the reaction of phenylalkanols with phosphoric acid was applied.[1] Starting with 5 g of the alcohol and 20 ml of phosphoric acid, 2 g of crude product was obtained which was distilled into two fractions. The first fraction distilled between 73 and 77° (4.8 mm) and weighed 1.2 g and the second fraction between 130 and 170° (0.6 mm) and weighed 1.2 g. The first fraction was analyzed by glpc, nmr, and ir before and after subjection to catalytic hydrogenation with hydrogen and palladium on carbon in ethanol; as expected from its boiling range, this fraction was found to contain all of the monomeric cyclidehydration and rearranged normal dehydration products. The results are summarized in Table I in the Discussion.

Reaction of 3-Methyl-3-(*p*-tolyl)-1-butanol (2) in Benzene and of 3-Methyl-3-phenyl-1-butanol in Toluene with Hot Phosphoric Acid.—In a typical experiment, the alcohol (1 g) was dissolved in the aromatic hydrocarbon (2 g) and the resulting solution was introduced through a pressure-equalizing dropping funnel into a reaction flask containing previously dehydrated phosphoric acid (5 ml). The flask was also equipped with a reflux condenser and with a thermometer immersed into the reaction mixture. The reactants were heated either in an oil bath kept at 230–240° or by using a direct flame for 15 min. At the end of this period, the mixture was left to cool, diluted with water, and extracted with ether. The ether layer was washed with water, sodium carbonate solution, and again with water, followed by drying over anhydrous sodium carbonate. The ether was distilled and the remaining liquid was analyzed by glpc. Comparison of the glpc data of the products from these crossover experiments with those of the products from the treatment of neat alcohols with phosphoric acid revealed the absence of crossed products in the resulting mixtures. Only products formed by intramolecular reactions were detected.

Registry No.—**2**, 27724-60-3; **4**, 16204-72-1; **7**, 27724-62-5; phosphoric acid, 7664-38-2.

(23) J. R. Owen and W. H. Saunders, *J. Amer. Chem. Soc.*, **88**, 5809 (1966).

(24) This was characterized by hydrolysis to *m*-methylcinnamic acid, mp 114–115°; W. V. Miller and Rhode [*Ber.*, **23**, 1899 (1890)] reported mp 115°.

(25) Characterized by hydrolysis to *m*-methylhydrocinnamic acid, mp 43–44°; W. V. Miller and Rhode [*ibid.* **23**, 1899 (1890)] reported mp 42–43°.

(26) On this column and on the three columns described in ref 9, the 1,1,5-trimethylindan (**5**) has a shorter retention time than 1,1,7-trimethylindan (**7**).