this temperature. The ultraviolet spectra of both solutions from 275 to 310 m$\mu$ were unchanged with respect to the spectra of the unheated samples except for small decreases in absorption. At least 75% of the cis-stilbene was still present after heating in both cases. trans-Stilbene absorbs much more strongly than cis-stilbene in this same ultraviolet region. There was no evidence for any trans-stilbene formation in either case.

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# A Cyclodehydration Synthesis of 2-Aryl-3-methylindenes[1a,b]

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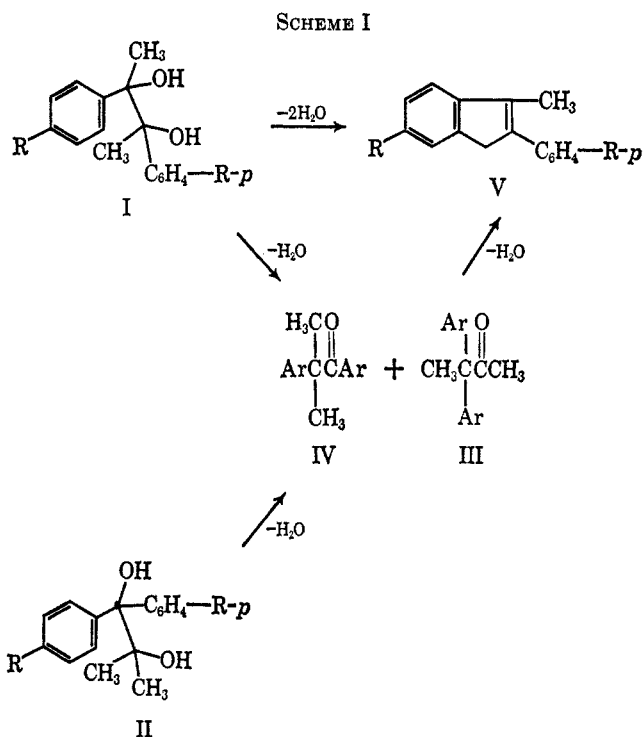Department of Chemistry, University of Delaware,
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The double dehydration of symmetrical alkyl aryl pinacols to olefinic hydrocarbons has been reported by numerous workers with a variety of conclusions as to the nature of the products. Variously cyclobutenes,[2] anthracenes,[3] butadienes,[4] and indenes[5] have been claimed. Careful work has established the existence of the butadienes[6] and indenes[7] and the presumed elimination of anthracenes and cyclobutenes as authentic reaction products.

Activated aryl groups bearing electron-releasing amino, dimethylamino, and hydroxyl substituents in the diaryl dialkyl pinacols have been found to undergo indene cyclodehydration with dilute acid catalysis.[5,8] These substituents presumably enhance the reactivity of the ring to electrophilic alkylation. With pinacols which are phenyl or p-tolyl members of the symmetrical diaryl dialkyl ethanediol family, mild acids produce only pinacol–pinacolone rearrangement.[9]

The utilization of polyphosphoric acid at elevated temperatures has provided a convenient synthesis of 2-aryl-3-methylindenes. In this fashion 32–39% yields of the unsubstituted, chloro-, methyl-, and phenyl-6-R-3-methyl-2-p-R-phenylindenes (V) (Scheme I) were obtained. The nmr spectra excluded the possibility of isomeric alternative cyclization products. The indenes showed characteristic methyl triplets at 2.2–2.5 ppm and methylene quartets ($J = 2$ cps) at 3.6–3.8 ppm.

It was observed that the identical indenes were available, although in somewhat poorer yields, by the polyphosphoric acid treatment of the monodehydration

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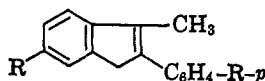
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SCHEME I



products of pinacols, i.e., pinacolones. Under comparable reaction conditions of time, temperature, and concentration, the parent pinacols were converted in greater percentage to indene product than were the pinacolones. It therefore appears that pinacolones are not obligatory intermediates in the cyclodehydration and that another mechanistic pathway, other than direct cyclization from diols to butadienes to indenes, as hypothecated by Allen and Corwin,[5] exists for ketonic intermediates.

The observation that $\beta$-benzpinacolone, structurally incapable of forming indene products, can undergo rearrangement in strongly acidic medium[10] can be used to support the view that pinacolones can protonate and rearrange. Thus pinacols, such as the symmetrical diaryl dialkyl ethanediols reported here, have the possibility of both a direct and an indirect (through protonated pinacolones) route to indene products.

In the case of the unsymmetrical pinacol, 1,1-di-p-tolyl-2-methyl-1,2-propanediol (II, R = $CH_3$) it appears that there is no appreciable direct closure from diol to indene but that in fact the pinacolone, 3,3-di-p-tolyl-2-butanone (III, R = $CH_3$), is the critical intermediate. See data in Table I.

TABLE I[a]

| Compd, R = $CH_3$ | Hours of contact | Rel % | | | % recovery[c] |
|---|---|---|---|---|---|
| | | Indene V[b] | Ketone IV | Ketone III | |
| I | 0.25 (200°) | 2.4 | 2.2 | 95 | 91 |
| | 3.50 | 39 | 27 | 31 | 72 |
| II | 0.25 | 3.2 | 14 | 83 | 73 |
| | 3.50 | 9.0 | 43 | 48 | 72 |
| III | 6.0 | 15 | 18 | 67 | 70 |
| IV | 5.0 | 1.1 | 94 | 4.0 | 84 |

[a] Nonequilibrium conditions; compound mixed with polyphosphoric acid and heated to 245–255° (exception as noted). [b] 3,6-Dimethyl-2-p-tolylindene. [c] Based on total moles of material isolated to total moles of starting compound. Polymeric resins were present in each reaction; for similar experiences, see ref 6.

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## TABLE II

### 2-ARYL-3-ALKYLINDENES



| R | Mp, °C | Yield, % | Formula | Calcd, % | | | Found, % | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | C | H | Cl | C | H | Cl |
| H | 74–75[a] | 36 | $C_{16}H_{14}$ | 93.16 | 6.84 | | 93.52 | 6.91 | |
| Cl | 118–119 | 39 | $C_{16}H_{12}Cl_2$ | 69.84 | 4.39 | 25.77 | 70.13 | 4.49 | 25.75 |
| $CH_3$ | 77–79 | 39 | $C_{18}H_{18}$ | 92.26 | 7.74 | | 92.23 | 8.07 | |
| $C_6H_5$ | 119–120 | 32 | $C_{28}H_{22}$ | 93.81 | 6.19 | | 94.08 | 6.05 | |

[a] Reported mp 76–78°; see ref 7.

The direct closure of II should lead to the formation of the 2-methyl-3-arylindene as the predominant product. We have found that on short contact (15 min) with polyphosphoric acid at 240°, 83% of the product mixture consisted of III, 14% of IV, and 3% of the indene V. No trace of 2,6-dimethyl-3-p-tolylindene was found. After 3.5 hr, the product mixture consisted of 9% indene V.

When 2-methyl-3-phenylindene was synthesized by the method of Mayer, Sieglitz, and Ludwig[11] and introduced into the reaction medium, it underwent an apparent double 1,2 shift to give rise to 2-phenyl-3-methylindene. The extended conjugation of the latter indene would lead to the expectation that it should be the more stable isomer. Indeed 3-phenylindene has been reported to rearrange to 2-phenylindene.[12]

The existence of this unusual migration makes it difficult to conclude whether the indene V arises by a direct cyclization of the unsymmetrical diol II followed by an instantaneous isomerization of the initial unstable indene, or whether pinacol–pinacolone rearrangement is the initial consequence and closure follows from the protonated pinacolones.

Because the unsymmetrical pinacol II is very susceptible to pinacol rearrangement, the initial carbonium ion would be stabilized by two phenyl systems, and because the 2-methyl-3-phenylindene is not quantitatively (63% only) isomerized to V after 3.5 hr of contact, it can be presumed that cyclization occurs predominantly through the nonconjugated pinacolone III (Scheme II). We have already demonstrated that this pinacolone is initially formed in very high yield during the polyphosphoric acid treatment.

One mechanistic possibility would be the acid-catalyzed enolization of III followed by attack on the aromatic ring by a protonated form of the enol double bond. Closure of similar phenylpropylenes to indanes has been demonstrated in acid medium.[13] The resulting indanol, in or proposed mechanism, would undergo loss of the protonated hydroxyl function, aryl migration, and deprotonation to give the final product.

For the maximum synthetic utility of the cyclodehydration as a preparative method for indenes, it was found preferable to add the diols to the polyphosphoric acid at 230° with continuous stirring of the reaction mixture. The temperature of the acid was then raised to 270–280° for approximately 3–4 hr. The results and analytical data for the indenes prepared are given in Table II.

Diols substituted with hydroxyl, methoxyl, amino, and dimethylamino groups in the para position of the phenyl rings were converted into polymeric resins by this method. Other procedures are available for the indene cyclodehydration of these compounds.[5,8]

### Experimental Section[14]

2,3-Diphenyl-2,3-butanediol,[3] 2,3-di-p-tolyl-2,3-butanediol,[15] and 2,3-di-p-chlorophenyl-2,3-butanediol[16] were synthesized by published procedures.

2,3-Di-p-biphenyl-2,3-butanediol was prepared by the aluminum amalgam bimolecular reduction of 4-acetylbiphenyl in benzene. The general procedure developed by Backer[15] for reduction of p-methylacetophenone was employed. A yield of 41% of white microcrystals, mp 241–241.5°, was obtained.

*Anal.* Calcd for $C_{28}H_{26}O_2$: C, 85.24; H, 6.64. Found: C, 85.26; H, 6.35.

### SCHEME II
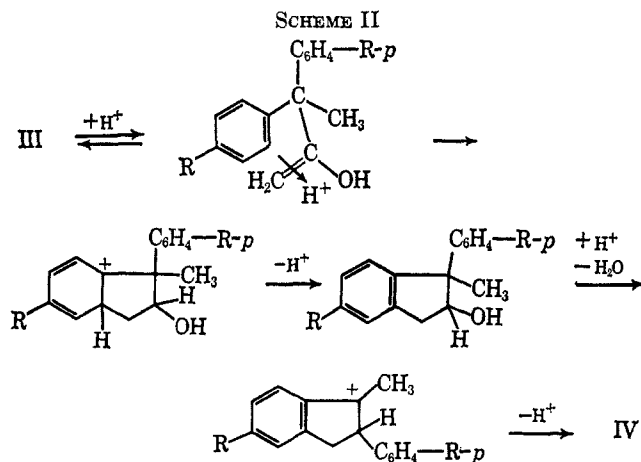
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(14) Gas chromatographic analyses were carried out on Aerograph Model A-350 (Wilkens Instrument and Research, Inc.) Dual columns (10 ft) consisting of either silicone oil GE-SF-96 coated 10% on firebrick or Apiezon-N coated 12% on Chromosorb were used. Ideal conditions were found to be linear temperature programming from 220 to 310° at 10°/min with helium flow rate of 50–55 cc/min.
Combustion analyses were performed by Dr. Alfred Bernhardt at the Max-Planck-Institut, Mülheim, Ruhr, and by Crobaugh Microanalytical Laboratories, Charleston, W. Va.
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1,1-Di-p-tolyl-2-methyl-1,2-propanediol (II) was synthesized by the addition of 0.20 mole of ethyl α-hydroxyisobutyrate to 0.58 mole of p-tolylmagnesium bromide in 900 ml of anhydrous ether. The ester was pretreated by shaking with 3 g of sodium hydride in 20 ml of ether and was then filtered directly into the dropping funnel. Following the dropwise addition of the ester solution to the mechanically stirred Grignard solution, the reaction mixture was refluxed for 2 hr and then stirred at room temperature overnight. After hydrolysis, ethereal extraction, and drying of the organic layer over magnesium sulfate, the concentrated oil was vacuum distilled. The material boiling at 184–187° (3.5 mm) (38.5 g of 72% yield) was taken as product. The product crystallized to colorless prisms, mp 78.5–80°.

*Anal.* Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 80.18; H, 7.98.

**3,3-Di-p-tolyl-2-butanone (III).**—Since product identification in the di-p-tolyl–dimethyl ethylene glycol system was carried out by peak enhancement gas phase chromatography, it was necessary to have available authentic samples of the possible pinacolones. The pinacolone rearrangement of 12.4 g of 2,3-di-p-tolyl-2,3-butanediol in 2.0 g of p-toluenesulfonic acid and 45 ml of glacial acetic acid was carried out by heating at reflux for 2.5 hr. After neutralization of the reaction mixture with aqueous sodium carbonate, ether extraction, and drying with sodium sulfate, the concentrated product layer was distilled under vacuum. Authentic III distilled at 197–200° (14 mm) (84% yield) and vpc analysis indicated that it was homogeneous. A single nonconjugated carbonyl at 1700 cm$^{-1}$ was observed in the infrared spectrum. A semicarbazone was prepared, mp 178°, from ethanol–water.

*Anal.* Calcd for $C_{19}H_{23}N_3O$: N, 13.57; Found: N, 13.41.

A 2,4-dinitrophenylhydrazone, recrystallized from methanol, melted at 145–146°.

*Anal.* Calcd for $C_{24}H_{24}N_4O_4$: N, 12.95. Found; N, 12.78.

**1,2-Di-p-tolyl-2-methyl-1-propanone (IV)** was prepared by the dialkylation of 4,4′-dimethyldesoxybenzoin[17] with freshly prepared potassium t-butoxide and methyl iodide. A solution of 0.22 mole of the ketone in 200 ml of benzene was added with vigorous stirring to 23.5 g of potassium dissolved in 300 ml of t-butyl alcohol and 80 ml of benzene. The deep orange solution which resulted was refluxed for 2 hr and 0.60 mole of methyl iodide was added. The reaction mixture was stirred overnight and then cooled in an ice–water bath. A rapid filtration of the cooled mixture removed the precipitated potassium iodide. The organic filtrate was hydrolyzed by the dropwise addition of cold water and the product layer was washed with a saturated saline solution. The organic phase was dried over sodium sulfate, concentrated under vacuum, and distilled. The fraction boiling at 142–144° (0.3 mm) (81% yield) was found to be chromatographically pure. Infrared analysis revealed a single conjugated carbonyl at 1670 cm$^{-1}$.

*Anal.* Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.98. Found: C, 85.58; H, 8.17.

**General Procedure for Indene Synthesis.**—The material (5–15 g) to be dehydrated was added in small portions to approximately 100 g of polyphosphoric acid being held at 210–230° in a sand or oil bath. The contents of the three-neck, round-bottom reaction vessel were stirred mechanically under a reflux condensor and the temperature of the acid was raised to 260–280° and held there for 3–4 hr. The dehydration was terminated by cooling the reaction mixture to 100° and pouring it onto a 10-volume excess of ice and water. The product was extracted into an ether–benzene layer. The aqueous phase was then neutralized with 40% potassium hydroxide solution and re-extracted with ether and benzene.

The combined organic extracts were washed with sodium carbonate solution until neutral, dried over sodium sulfate, filtered, and concentrated under vacuum. The indenes could usually be isolated by addition of cold methanol to the concentrated organic phase which induced the precipitation of the hydrocarbons. In the cases in which this technique failed, the indenes could be separated by preparative gas chromatography.

When 2-methyl-3-phenylidene[11] was treated by this procedure it was converted into a mixture of 63% 2-phenyl-3-methylindene and 32% unreacted starting material after 3.5 hr of contact. Indene separation was accomplished on the Apiezon N column under the conditions described.

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# Cleavage Reaction of 2-Butenyloxy Derivatives with Potassium t-Butoxide

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The base treatment of β,γ-unsaturated systems (I) (ethers, amines, sulfides, sulfoxides, sulfones, esters, ketones, and nitriles) has been reported to result in partial or complete isomerization to the corresponding α,β-unsaturated systems (II) or elimination and in some cases both types of reactions.

$$R—CH=CH—CH_2—X \qquad RCH_2—CH=CH—X$$
$$I \qquad\qquad\qquad\qquad II$$

Virtually complete isomerization of the unsubstituted β,γ isomers I [R = H; X = $-OC_6H_5$, $-S-C_6H_{13}$, $-N(CH_3)_2$] to the corresponding α,β isomers occurred readily with potassium t-butoxide in DMSO or DME[1] (1,2-dimethoxyethane). In addition, similar observations were noted for unsubstituted β,γ-unsaturated ethers using alkoxide catalysts without a solvent.[2] It has also been known for some time that the base-induced equilibria between I (R = H; X = $-CN$, $-COOH$, $CO_2^-$, $-COOC_2H_5$, $O=CCH_3$) and the corresponding α,β isomers II predominantly favor the latter.[3] However, a shift in the equilibria to favor the β,γ isomers was noted when the analogous γ-substituted compounds I (R = $CH_3$ or alkyl) were subjected to base treatment.[3] More recently, O'Connor and Lyness[4] similarly observed a predominance of the β,γ isomer in a study of the base-catalyzed equilibria of unsaturated sulfur derivatives I (R = alkyl; X = $-SOCH_3$, $-SO_2CH_3$). In the case of the γ-substituted sulfide I (R = $CH_3$ or alkyl; X = $-SOCH_3$), both equilibration to a mixture of the β,γ isomer I (34%) and the α,β isomer II (66%) and 1,4-diene elimination was observed.[4b] The reactions of cyclic butadiene sulfone[5] and 1-O-heptadec-2-enyl-2,3-O-isopropylidene glycerol ether[6] with base have only been reported to involve diene elimination.

Among the numerous isomerization studies of unsaturated systems described above, only one involved a study of the reaction of a γ-substituted β,γ-unsaturated ether with base. In this report, diene elimination was observed from the alkenyl glycerol ether; however, there was no indication of whether or not isomerization had occurred.[6] As part of our continuing studies of the chemistry of ortho esters, we investigated the base-catalyzed isomerization reaction of tri-2-butenyl orthoformate (III) and also that of a related system, phenyl-2-butenyl ether (IV). The reactions of III and IV with catalytic or molar quantities of potas-

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