TABLE II

ISOMERIZATION OF GAS *vs.* RESIDUE FROM TBP PYROLYSIS

Pyrolysis temp. ±2°	TBP decompn.,[a] %	Residual butyls, %	Substance isolated and dealkylated with HBr	Residual alkyl composition, %		*sec*-Butyl yield,[b] %	Butene-2 (*cis* + *trans*) yield,[c] %	Butene-2/ *sec*-butyl	C–O scissions/ *sec*-butyl
				n-Butyl	*sec*-Butyl				
242	72	28	Pot residue	97.2	2.8	0.78	18	23	92
221	70	30	H_2MBP	97.2	2.8				
			HDBP	97.3	2.7				
			Pot residue	97.1	2.9	0.87	17	20	80
223	47	53	Pot residue	99.2	0.8	0.4	6.9	17	117
221	30	70	HDBP	99.6	0.4				
			TBP	99.8	0.2				
			Pot residue	99.7	0.3	0.2	2.3	12	150

[a] All butyl groups removed = 100% decomposition. [b] Based on TBP before pyrolysis. [c] Per cent TBP decomposed × 0.82[d] × butene-2 fraction.[e] [d] Average yield of butenes from TBP pyrolysis (ref. 2b). [e] Obtained from data in Tables I and II (ref. 2b).

Turkevich and Smith[7] to exchange hydrogen atoms with olefins; an unstable complex must have formed. The H_3PO_4-catalyzed isomerization of butenes has been explained by Haag and Pines[8] as the rearrangement of a secondary carbonium ion intermediate to a π-complex, followed by rapid loss of a proton. Since in the pyrolysis of the TBP the butene was being removed from the reaction vessel as it was formed, the chance for recombination was therefore lessened. No butyl ester of phosphoric acid has apparently been isolated from a butene–H_3PO_4 reaction.

Perhaps more rearrangement occurred in the following way. Acid attack on the esters at elevated temperatures caused carbon–oxygen bond fission; the resulting intermediate, whether a primary carbonium ion or a π-complex, could then rearrange to the more stable secondary carbonium ion or π-complex by hydride shift.[9] Recombination may then have taken place by nucleophilic attack of the acid on the electron-deficient carbon. However, since phosphoric acid esters are weak nucleophiles, the preferred reaction path was proton elimination to give *cis*- or *trans*-butene isomers. The faster dealkylation rate of the *sec*-butyl phosphates in comparison with the *n*-butyl phosphates also hindered the buildup of *sec*-butyl groups in the residue.

Experimental

Ester interchange between TBP and anhydrous H_3PO_4 and recovery of the TBP after reaction were done as before.[3]

TBP was decomposed thermally[2] to varying extents up to 72%. Individual components were isolated from the pot residues; the acids were neutralized and the TBP was removed by ether or carbon tetrachloride extraction. The aqueous salt solution was cooled in ice and reacidified with concentrated sulfuric acid; H_2MBP and HDBP were then separated by countercurrent batch extraction.[10] The H_2MBP was finally isolated by continuous extraction with ether.

Samples of the products, pot residues, and starting material were dealkylated by refluxing 48% HBr.[4] A 50-ml., round-bottomed flask served as reaction vessel for 1–5 g. of sample and 10–25 ml. of acid. The butyl bromides formed were distilled through an 11-cm. Vigreux column. Each dealkylation required 0.5 to 0.75 hr. Yields were >95%.

Purity was determined by gas chromatography at 100°. A 1-m. column of 23% dinonyl phthalate (3 g./10 g. of 30–50 mesh Celite) was swept at a flow rate of 50 cc. of helium per minute. The small peak having the retention time common to *sec*-butyl bromide and isobutyl bromide was found by the method of Harris and McFadden[11] to result only from *sec*-butyl bromide. The *sec*-butyl bromide reacted with the silver nitrate at room temperature and no peak was found at the retention time of *sec*-butyl bromide on the 1-m. dinonyl phthalate column in series at 100°. Correction was made for the small amount of isomerization occurring during the dealkylation reaction by running a blank on pure TBP.

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Synthesis of 5- and 6-Methoxyindene[1]

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In a study of tautomerism in derivatives of indene, Ingold and Piggott[2] reported that distillation of either the 5- or the 6-methoxy isomers of 1-indanamine hydrochloride led to the formation of but a single methoxyindene. From this they concluded that indene possesses a mobile tautomeric system. However, Koelsch and Scheiderbauer[3] were able to isolate 5- and 6-indenyloxyacetic acids, thus providing the first evidence that the nonbenzenoid double bond of indene occupies a fixed position. Since then, abundant evidence has accumulated,[4–7] particularly from the work of Bergson and Weidler,[8–11] that tautomeric forms of monosubstituted indenes can exist separately. Nonetheless, in the most recently reported attempt to prepare 5-methoxyindene, Panetta and Bunce[12] found that reduction and dehydration of 5- and 6-methoxy-1-indanone led to the same product. They

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[1] This work was supported by U. S. Public Health Service Grant 5 R01 MH 07575 and National Institutes of Health Graduate Training Grant 5-T1-GM-107.

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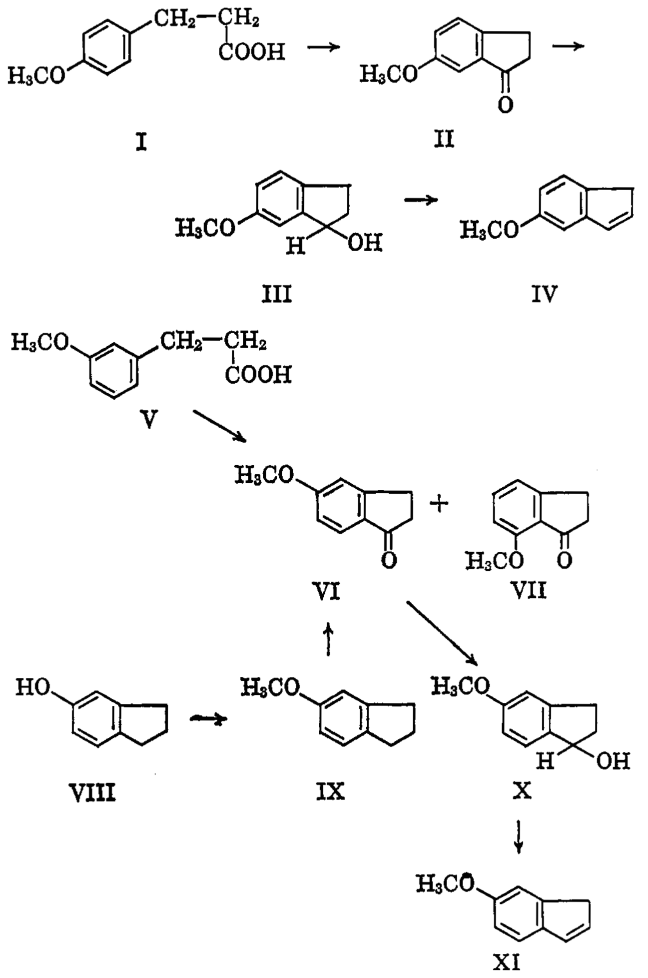
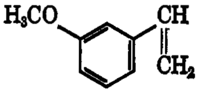
suggested that this product was probably 6-methoxyindene, which they believed to be the more stable isomer. However, no chemical evidence was presented in support of this suggestion. Süs and co-workers[13] have reported the isolation of 5-methoxyindene prepared by decarboxylation of 6-methoxy-1-indancarboxylic acid. No structural proof was provided.



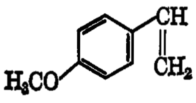
In this report, the synthesis of chemically distinct 5- and 6-methoxyindenes is described. 1-Indanones substituted in the aromatic ring were prepared from β-methoxyphenylpropionic acids by the cyclodehydration method of Uhlig[14] according to the procedure of Bone and Cort.[15] The 5- and 6-methoxyindanones were reduced with lithium aluminum hydride and the resulting indanols were dehydrated with p-toluenesulfonic acid. Such dehydration has been shown not to cause isomerization of the monomethylindenes.[5]

5-Methoxyindene was obtained as a colorless liquid which was quite stable at room temperature. In contrast, 6-methoxyindene was found to be a white solid which decomposed slowly to a yellow liquid even when stored under nitrogen in the cold. The nature of the decomposition products was not determined.

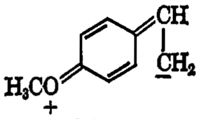
Elemental analysis established that the products IV and XI were isomers. That they were not identical was demonstrated by comparison of their ultraviolet, infrared, and n.m.r. spectra and by thin layer chromatography (t.l.c.). The isomers were readily separable on alumina or silica gel with each isomer moving as a single spot. Support for the structural assignments came from the ultraviolet spectra. Compounds IV and XI are analogs of 3-vinylanisole (XII) and 4-vinylanisol (XIII), respectively. Joy and Orchin[16] have reported that the absorption maximum at 250 mμ in XII (log ϵ 4.04) is shifted to 260 mμ in XIII (log ϵ 4.17). This shift may be explained on the basis of the contribution of resonance form XIIIa to the structure of XIII. Such a resonance form cannot be written for XII. The ultraviolet spectra of 5-methoxyindene [λ_{max} 252 mμ (log ϵ 3.69)] and 6-methoxyindene [λ_{max} 268 mμ (log ϵ 4.02)] show an analogous shift which may be explained by the contribution of resonance form XIa to the structure of 6-methoxyindene.



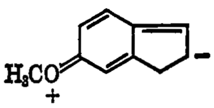
XII



XIII



XIIIa



XIa

Because of the known ability of monosubstituted indenes to undergo tautomeric rearrangements,[7,10] we wished to know if there was any cross-contamination between products IV and XI. The most sensitive means for this determination proved to be thin layer chromatography. The method of Kucharczyk and co-workers[17] was used to detect the methoxyindenes. Pure samples of IV and XI were shown to be uncontaminated with each other within the limits of sensitivity of the method (less than 0.1%).

Attempts were made to induce isomerization of IV and XI. Methods known to cause isomerization of other monosubstituted indenes were employed.[3,10] Boiling with 5% potassium hydroxide for 15 min. had no effect detectable with t.l.c. Likewise, exposure to triethylamine in pyridine for 4 days at room temperature produced no interconversion of either isomer. These results, which indicate that IV and XI are relatively stable forms, are in contrast with those of Panetta and Bunce.[12] Using routes which would be expected to yield the two isomers, these workers obtained but a single product. Thermal isomerization of monosubstituted indenes has been reported at temperatures as low as 164°.[7,18] Insofar as Panetta and Bunce had accomplished dehydration at temperatures in excess of 220°, thermal isomerization might have taken place. To test this possibility, a sample of 5-methoxy-1-indanol was dehydrated by distillation at atmospheric pressure from crystals of potassium bisulfate. The distillate thus obtained was shown on t.l.c. to be a mixture of IV, XI, and an unidentified product. 6-Methoxyindene was also present in the residue in the

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[16] J. R. Joy and M. Orchin, *J. Am. Chem. Soc.*, **81**, 305 (1959).

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distilling flask, but no 5-methoxyindene was detectable in this residue.

To ascertain the importance of potassium bisulfate to this isomerization, authentic samples of IV and XI were allowed to distil at bath temperatures of 220–240° for 30 min. both in the presence and in the absence of potassium bisulfate. The results in all cases were the same. The distillate was a mixture of the starting material and its isomer. Only the isomer originally present could be detected in the residue. It thus appears that any synthesis of 5- or 6-methoxyindene which involves distillation of the final product at atmospheric pressure will lead to mixtures of the two isomers. The results of previous workers[2,12] may be explained on this basis.

Experimental

General.—Melting points were taken on a Kofler micro hot-stage apparatus (A. H. Thomas Co.) and are corrected. Infrared spectra were determined with a Perkin-Elmer Infracord spectrophotometer. Ultraviolet spectra were recorded on a Beckman Model DB spectrophotometer. N.m.r. spectra were obtained with a Varian A-60 high resolution n.m.r. spectrometer. The samples were run in carbon tetrachloride solution using tetramethylsilane as an internal reference standard and the chemical shifts are reported as τ values. Microanalyses were performed by the Galbraith Laboratories, Inc., Knoxville 21, Tenn. Thin layer chromatograms were run on silica gel G and aluminum oxide G (both from Research Specialties Co., Richmond, Calif.) with benzene–carbon tetrachloride (1:1). The spots were located with a spray made by mixing 0.2 ml. of a 37% solution of formaldehyde with 10 ml. of concentrated sulfuric acid.[17] With this developing agent, 5-methoxyindene gave a blue-green color while 6-methoxyindene gave a purple-violet color.

6-Methoxy-1-indanone (II).—This ketone was prepared according to Bone and Cort.[15] The polyphosphoric acid was prepared by dilution of 500 g. of commercial polyphoshoric acid (82–84% P_2O_5) with 120 g. of 85% phosphoric acid. II was obtained as white needles in 27% yield, m.p. 109–111° (lit.[15] m.p. 108–109).

6-Methoxy-1-indanol (III).—A solution of 2.5 g. (0.015 mole) of II in 176 ml. of dry ether was heated under reflux for 1 hr. with 0.27 g. of lithium aluminum hydride. The mixture was cooled, excess $LiAlH_4$ was destroyed with water, and the mixture was filtered through Celite. The filtrate was dried with sodium sulfate and the solvent was removed to yield a clear, slightly yellow liquid which gives a white solid (2.4 g., 95%) after storage overnight at −15° under nitrogen. Crystallization from *n*-hexane gives white crystals of 6-methoxy-1-indanol (2.1 g., 81%), m.p. 47–48.5°.

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37. Found: C, 73.21; H, 7.34.

5-Methoxyindene (IV).—A solution of 2.5 g. (0.015 mole) of III in 73 ml. of dry benzene was heated under reflux for 30 min. with 0.2 g. of *p*-toluenesulfonic acid. The mixture was cooled, water was added, and the phases were separated. The water phase was extracted with ether. All organic phases were combined and dried with sodium sulfate, and the solvent was removed to give a tan liquid (2.3 g., 100%). Distillation at 110–145° (10 mm.) yielded 5-methoxyindene as a colorless liquid (1.2 g., 54%): infrared (liquid film) 1550, 1118, 1107, 1070, 948, 843, 730, 639 cm.$^{-1}$; λ_{max} (absolute ethanol) 252 mμ (log ϵ 3.69); n.m.r. τ 7.83 (methylene protons), 6.40 (methoxy protons), 3.68–2.69 (vinyl protons overlapping aromatic protons). IV was homogenous on thin layers of silica gel or alumina with R_f 0.63 and 0.93, respectively.

Anal. Calcd. for $C_{10}H_{10}O$: C, 82.16; H, 6.90. Found: C, 81.81; H, 6.79.

5-Methoxy-1-indanone (VI). Method A.—The ketone was prepared as directed by Bone and Cort.[15] The polyphosphoric acid was prepared as in the synthesis of II. VI was obtained as white crystals in 26% yield, m.p. 109–110.5°. (lit.[15] m.p. 108°).

Method B.—The ketone was prepared according to the method of Panetta and Bunce.[12,19] The product had m.p. 110–110.5° (lit.[12] m.p. 108.4–109.4°). The infrared spectrum of this product was identical with the ketone produced by method A. A mixture melting point of the two products showed no depression.

5-Methoxy-1-indanol (X).—A solution of 4.8 g. (0.028 mole) of VI was heated under reflux in 340 ml. of dry ether with 1.0 g. of lithium aluminum hydride. The 5-methoxy ketone was found to be more resistant to reduction than was the 6-methoxy ketone, the former requiring 4 hr. for complete reduction. The reaction mixture was then treated as described for 6-methoxy-1-indanol. The crude product contained no 6-methoxyindene, but distillation at 115–140° (0.02 mm.) gave 5-methoxy-1-indanol which was contaminated with the indene.

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37. Found: C, 75.42; H, 7.37.

6-Methoxyindene (XI).—A solution of 1.59 g. (0.097 mole) of X was heated under reflux in 47 ml. of dry benzene for 30 min. with 0.13 g. of *p*-toluenesulfonic acid. The mixture was then treated as above for 5-methoxyindene to yield a thick, yellow liquid (1.53 g., 96%). This was dissolved in petroleum ether (b.p. 30–60°) and cooled to −15° under nitrogen. After 2 days a white solid separated. Three recrystallizations from petroleum ether gave pure 6-methoxyindene (0.49 g., 32%): m.p. 46–47°; infrared (Nujol) 1093, 875, 823, 738 cm.$^{-1}$; λ_{max} (absolute ethanol) 268 mμ (log ϵ 4.02); n.m.r. τ 6.87 (methylene protons), 6.35 (methoxy protons), 3.65–2.85 (vinyl protons overlapping aromatic protons, definitely different from the corresponding pattern in IV). XI was homogeneous on thin layers of silica gel and alumina with R_f 0.28 and 0.84, respectively.

Anal. Calcd. for $C_{10}H_{10}O$: C, 82.16; H, 6.90. Found: C, 82.01; H, 6.69.

Attempted Isomerization of 5- and 6-Methoxyindene.—Indene solutions (2 *M*) in pyridine were treated with 1.08 *M* triethylamine as catalyst at 26–28° for 4 days. Periodically, aliquots were removed and chromatographed on silica gel. No isomerization could be detected.

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Methylation of Simple Unsaturated Hydrocarbons by Dimethyl Sulfoxide

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Although dimethyl sulfoxide (DMSO) has been used extensively as a solvent medium, it is only quite recently that it has been recognized that the DMSO itself participates in a number of base-catalyzed reactions. The hydrogens are quite labile, and exchange between these and weak organic acids is readily measured.[2] Preparation of the methylsulfinyl carbanion was reported by Corey.[3] The addition of this carbanion to various unsaturated bonds has been ob-

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