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INDENOLS IN COAL TARS

THE FIRST PREPARATION OF INDENOL[1a]

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Abstract—Recent work has disclosed that indenols are present in coal tars, but, until the present, no indenol has been isolated or synthesized. The first members of this class of reactive compounds have now been synthesized by catalytic dehydrogenation of indanols at 650° over chromia alumina with nitrogen gas as carrier. The indenols have been isolated as white, crystalline, rather stable, solids. Dehydrogenation of 4-indanol yields 4- and 7-indenol; 5- and 6-indenols are obtained similarly from 5-indanol. Separation of the indenols from starting indanol in each case was effected by ligand exchange chromatography. Each pair of indenols was then separated by gas chromatography. The 4- and 7-indenols prepared in this way were characterized by UV, IR and NMR spectra.

INDANOLS have long been known to be major constituents of coal tar, but only recently evidence of the presence of indenols has been gained from examination of several coal tars by low ionizing voltage mass spectrometry.[2,3] This evidence is based on the appearance of a series of peaks at mass units corresponding to the mol. wts of indenol and its homologues in coal tar phenolic fractions. This series of peaks parallels the corresponding indanol series of mass unit peaks.

While indenes and indanols are readily available, simple indenols have escaped both synthesis and isolation. Two derivatives of indenol, an indenol-O-acetic acid[4] and a methoxyindene[5] have been reported, but no reference exists for the preparation of the parent phenol. (1-Indenol is known, but this is an alcohol, not a phenol.) A 2,3-disubstituted-6-indenol has been reported;[6] this compound, 3-ethyl-2-p-hydroxyphenyl-6-hydroxyindene, has its indene system stabilized by the substituents on the 5-membered ring.

To study the properties of the indenols, and to confirm their presence in coal tar, it appeared necessary to isolate or synthesize at least one member of the series. The synthetic approach proved to be more rewarding.

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[2a] A. G. Sharkey, Jr., G. Wood, J. L. Shultz, I. Wender and R. A. Friedel, *Fuel* **38**, 315 (1959);
[b] R. E. Dean, E. N. White and D. McNeil, *J. Appl. Chem.* 629 (1959).

[3] C. Karr, Jr., P. A. Estep and L. I. Hirst, Jr., *Analyt. Chem.* **32**, 463 (1960), reported the identification of 4- and 5-indenols in a coal tar fraction. The samples which they used for comparison were provided by us at an early stage in the development of this preparation. Unfortunately, these samples were impure and contained the indenols as minor constituents. As a result, the spectral evidence reported in the present paper fails to confirm the identifications reported by Karr *et al.*

[4] C. F. Koelsch and R. A. Scheiderbauer, *J. Amer. Chem. Soc.* **65**, 2311 (1943).

[5] C. K. Ingold and H. A. Piggott, *J. Chem. Soc.* **123**, 1469 (1923).

[6] M. Silverman and M. T. Bogert, *J. Org. Chem.* **11**, 34 (1946).

We have developed a procedure for preparing both 4- and 5-indenol by catalytic dehydrogenation of the respective indanols. Initially, a procedure developed by Webb and Corson[7] for the dehydrogenation of substituted ethylbenzenes to the corresponding styrenes was tried. The method involves passing steam and indanol over a chromia-alumina catalyst at 570°. The procedure was not reproducible, and analysis of the product by mass spectrometer and gas chromatograph showed that unchanged indanol was usually the major constituent.

Subsequently, this procedure was modified, resulting in higher and more reproducible yields. In addition, several techniques were developed for purifying the product. In the dehydrogenation itself, nitrogen was substituted for steam as a carrier gas and the pyrolysis temperature was increased to 650°. In this way, we prepared sizable quantities of indenols in good yields from both 4- and 5-indanol. The same procedure was used to dehydrogenate trimethylsiloxyindanes to the corresponding trimethylsiloxyindenes. This latter method is more convenient, since the trimethylsilyl ethers are liquids and thus more readily fed to the pyrolysis column. In addition, the ethers give somewhat better conversions to the dehydrogenation products.

Gas chromatography of the indenols as their trimethylsilyl ethers has certain advantages. In general, the ethers can be chromatographed at lower column temperatures than the parent indenols. The nonpolar nature of the ethers is an additional advantage, allowing a wider choice of column packing and giving better separation and less tailing of peaks. The trimethylsiloxyindenes appear to be more stable during storage than are the indenols.

Both the indanol and indenol trimethylsilyl ethers are readily prepared by refluxing the phenols with hexamethyldisilazane,[8] and the indenols are easily regenerated from the ethers by refluxing with ethanol.

The initial isolations of pure indenols required repeated recrystallizations from petroleum ether to obtain indanol-free samples. Purity was readily determined by gas chromatographic analysis, and checked by low ionizing voltage mass spectrometry which gives a measure of the ratio of mass 132 (indenol) to 134 (indanol). Subsequently several chromatographic procedures were developed which allowed complete separation of indenol from indanol.

The best separation used a ligand exchange[9] column containing a silver nitrate impregnated Dowex cation exchange resin. An indanol-indenol mixture in acetone was poured onto the column. Elution with petroleum ether removed the indanol. The indenol was eluted with chloroform. When the column was deliberately overloaded with indenol, the excess came off with the indanol, resulting in indenol containing less than 1 % indanol. This proved to be the best way to obtain indenol samples free of indanol.

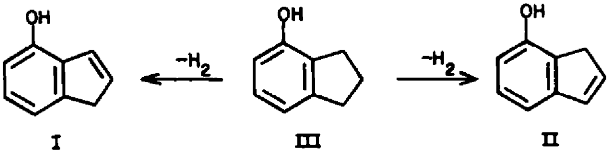
Dehydrogenation of an indanol does not produce a single product, since the indenol trimethylsilyl ethers are readily resolved in each case into two gas chromatographic peaks. The dehydrogenation products from 4-indanol were separated to give two different peaks, which have the same mass and almost identical UV spectra, but different IR spectra. These two compounds are undoubledly the isomeric 4-indenol (I) and 7-indenol (II), both of which can be formed by dehydrogenation of 4-indanol

[7] G. A. Webb and B. B. Corson, *Ind. Eng. Chem.* **39**, 1153 (1947).

[8] S. Friedman, M. L. Kaufman, W. A. Steiner and I. Wender, *Fuel* **40**, 33 (1961).

[9] F. Helfferich, *Nature, Lond.* **189**, 1001 (1961).

(III). The individual isomers appear to be stable with respect to each other at room temperature, but not at elevated temperature. If the gas chromatograph injection port temperature is kept below 200°, no isomerization of either isomer takes place. However, at injection port temperatures above 200°, isomerization occurs to give a mixture of the two. The extent of isomerization, up to an apparent equilibrium value, is a function of the inlet temperature. This is shown graphically in Fig. 1,[10] where the gas chromatographic behaviour of the trimethylsilyl ether of peak #1 is shown upon reinjection under different conditions.[11] The symmetrical shape of the peaks indicates that isomerization is not taking place on the column itself.



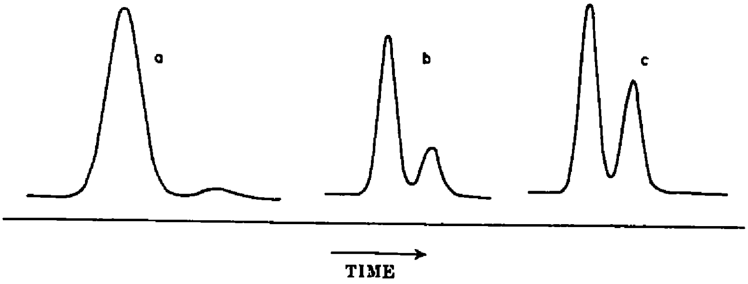


FIG. 1. --Gas chromatograms of the same sample of 7-trimethylsiloxyindene under different instrument conditions, showing thermal isomerization to 4-trimethylsiloxyindene.

	Column temp	External injection port temp	Heater power setting in arbitrary divisions	Estimated cartridge heater temp
a	145°	164°	70	
b	169°	171°	85	~290°
c	171°	203°	99	~325°

A study of the UV and NMR spectra of the two isomers leads to an assignment of the 7-indenol structure to the first component and 4-indenol to the second component. PMR spectra of both compounds have been obtained and compared[12] with the published NMR data for indene[13] and 4- and 7-methylindenes.[14] Both indenols have spectra similar to that of indene, consisting of aromatic proton resonances at low field, olefinic proton resonance at slightly higher field, a strongly concentration dependent

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[10] This technique has been used to obtain large quantities of peak #2 for isolation. This amounts to using the injection port as a microreacter.

[11] *cis-trans* Isomerization of olefins in a flash heater have been reported. L. J. Morris, R. T. Holman and K. Fontell, *J. Lipid Research* **1**, 412 (1960).

[12] R. A. Friedel and H. L. Retcofsky, unpublished work.

[13] D. D. Elleman and S. L. Manatt, *J. Chem. Phys.* **36**, 2346 (1962).

[14] J. A. Elvidge and R. G. Foster, *J. Chem. Soc.* 590 (1963).

hydroxyl resonance, and a methylene signal at much higher field. These are in the expected ratio of intensities; i.e., 3:2:1:2. The olefinic protons give rise to two double triplets as a result of coupling between the proton, its neighboring olefinic proton, and the methylene protons. The methylene protons produce an overlapping double doublet which appears as a triplet. Long range couplings add to the spectral line widths.

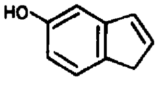
In 7-methylindene, the methylene proton resonance is shifted 9 c/s to lower field than in indene or 4-methylindene as a result of the absence of the 7-proton, and the signal is better resolved.[14] The same differences are found in the spectra of the two indenol isomers. Similarly, substitution of a methyl group at the 4-position perturbs the olefinic signal at the 3-position, and this difference is also found in the indenol spectra.

In the UV, the two longer wavelength bands are 60 to 70 Å longer in 4-indenol (OH conjugated with the olefinic bond) than in 7-indenol (OH not conjugated). This is analogous to *o*- and *m*-phenylphenol, where the isomer with the OH conjugated with the phenyl group (*o*-) absorbs at higher wavelengths than the isomer with the nonconjugated OH (*m*-).

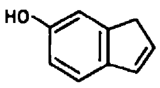
Treatment of either of the isomers (4- or 7-indenol) with triethylamine in pyridine at room temperature according to the procedure of Bergson and Weidler[15] brought about isomerization to an equilibrium mixture of the two isomers which was complete after approximately 2½ hr. A pyridine solution of either isomer was unchanged after 2 hr.

Isomerization of 7-indenol did not occur when it was treated with a benzene solution of *p*-toluenesulfonic acid at room temperature. Extensive polymerization did take place, however.

This isomeric pair phenomenon also has been found in the product of dehydrogenation of 5-indanol. The 5-indenol (IV) and 6-indenol (V) are less readily separated by gas chromatography, and have not as yet been resolved in quantities large enough for spectral studies. UV, mass, PMR and IR spectra of the mixture of IV and V are all consistent with the indenol structure.



IV



V

EXPERIMENTAL

The 4- and 5-indanols were obtained from Aldrich Chemical Co. and Rutgerswerke A.G. (Germany).

The chromia-alumina catalyst, #179 CP-1, was generously provided by the Houdry Process Corp. It was activated by heating it to 650° in the reactor column while a stream of N_2 which contained approximately 0·5% O_2 was passed through the column.

The UV spectra were obtained in cyclohexane; the IR spectra were done as KBr pellets. Ultimate analyses (macro) were done by the Analytical Group, Pittsburgh Coal Research Center, U.S. Bureau of Mines.

[15] G. Bergson and A. -M. Weidler, *Acta Chem. Scand.* 17, 862 (1963).

Design of pyrolysis column. The column used for dehydrogenation of indanols is a stainless steel tube, 100 cm long, with an O.D. of 25 mm. The lower 90 cm of the tube is wrapped with 33 ft of #20 B & S nichrome wire covered with porcelain insulator beads. The furnace portion of the tube is jacketed by a piece of asbestos pipe insulation. To the bottom of the tube is welded an outlet tube of 8 mm O.D. stainless steel leading to one or more cold traps by means of rubber tubing. The top of the column has a rubber stopper containing a needle-valve controlled addition funnel, a stainless steel thermocouple well extending approximately 50 cm into the tube, and a hypodermic needle for admitting N_2. The packing consists of a lower layer (10 cm) of glass beads, a layer of catalyst approximately 60 cm in length, and a top layer of glass beads. Preheating tapes are wound around the top 10 cm of the tube and also around the addition funnel.

Preparation of 4-trimethylsiloxyindane. A solution of 20 g of 4-indanol in 30 ml of hexamethyldisilazane was refluxed overnight under N_2. The excess hexamethyldisilazane was removed by distillation and the trimethylsilyl ether distilled (b.p. 86–88° at 5 mm).

Dehydrogenation of 4-trimethylsiloxyindane. While a stream of N_2 was flowing through the pyrolysis column, 30 g of 4-trimethylsiloxyindane was allowed to drip onto the column at a rate of 30 g per hr. The column temp was kept at 650°. The product was collected in a trap, which contained a mixture of benzene and pet. ether cooled in ice water. The solvent was evaporated from the trap contents to yield over 25 g crude product. Gas chromatographic examination showed the presence of some 4-indanol (as its trimethylsilyl ether) as well as traces of solvent. The major portion of the material appeared to be 4- and 7-indenols (as their trimethylsilyl ethers). This was confirmed by mass spectrometric analysis.

A portion of the crude trimethylsiloxyindene was refluxed overnight in ethanol to hydrolyze it to the indenol. The indenol was recrystallized from CCl_4 and from pet. ether to give needles, m.p. 77·5–79·0°. (Found: C, 82·07; H, 6·46. C_9H_8O requires: C, 81·79; H, 6·10%).

A sample of this indenol was converted to its trimethylsilyl ether for gas chromatographic analysis. This showed the complete absence of indanol. Two gas-chromatographically separable components were present in a ratio of about 4 to 1.

Dehydrogentaion of 5-trimethylsiloxyindane. In a similar manner, a mixture of 5- and 6-trimethylsiloxyindene, having a gas chromatographic peak ratio of 4 to 3, was prepared by dehydrogenation of 5-trimethylsiloxyindane (b.p. 97-99° at 6–7 mm). The material was converted to the indenol by refluxing in ethanol.

Dehydrogenation of 5-indanol. While a stream of N_2 was flowing through the pyrolysis column, molten 5-indanol was dripped onto the column at a rate of 30 g per hr with the column temp at 650°. The product was collected in an ice cooled trap. Gas chromatographic examination of the trimethylsilyl ethers of the product showed it to be largely 5- and 6-indenols.

Preparation of ion exchange column containing Ag^+. A chromatographic column was filled with 200 g of 50–100 mesh Dowex 50–X8 cation exchange resin. An $AgNO_3$aq containing 95 g $AgNO_3$ was poured through the resin filled column. The resin was washed with water and then air-dried. The Ag impregnated resin was packed into the chromatographic column.

Separation of 5-indanol and 5(6)-indenol. A mixture containing 2 g 5-indanol and 5(6)-indenol was dissolved in a minimum amount of acetone and poured into the prepared column which had been wet with 60–68° pet. ether. Elution was carried out with pet. ether. Gas chromatographic examination of the eluate showed that only 5-indanol was present. Elution with $CHCl_3$ removed the 5(6)-indenol, along with a small quantity of 5-indanol.

When larger amounts of indenol were put on the column, some indenol eluted with the indanol fraction. Elution with $CHCl_3$ then gave pure indenol, m.p. 78·0–79·5°. (Found: C, 81·92; H, 6·20. C_9H_8O requires: C, 81·79; H, 6·10%), λ 2580 Å, 2680, 2850, 2920, 2965, 3038; 3·20 μ (s), 5·40 (w), 5·55 (w), 5·87 (w), 6·18 (m), 6·28 (s), 6·46 (m), 6·75 (m), 6·90 (m), 7·34 (s), 7·48 (m), 7·61 (w), 7·68 (w), 7·81 (w), 7·95 (m), 8·16 (s), 8·25 (sh), 8·42 (w), 8·51 (m), 8·82 (m), 8·88 (w), 9·03 (m), 9·42 (m), 10·52 (m), 10·78 (s), 11·08 (m), 11·69 (s), 11·92 (w), 12·27 (s), 12·48 (w), 13·09 (m), 13·60 (m), 14·38 (s).

Gas-liquid chromatography of trimethylsiloxyindenes. Complete separation of trimethylsiloxyindenes and trimethylsiloxyindenas was achieved on a 150-ft × 0·01 in I.D. capillary column coated with a polypropylene glycol. This capillary column was mounted in a Perkin-Elmer 154 Gas Chromatograph equipped with a H_2-flame ionization detector. The conditions used to obtain this separation were: column temp, 151°; injection port temp, 212°; inlet press. of N_2 carrier gas, 18 psi gauge.

In addition, larger samples were run on a column made from a piece of Cu tubing, 610 cm long ×

0·30 cm I.D., coiled as a helix, and containing 12·4 g packing, made up in the wt ratio of 8 parts of D.C. 550 silicone oil to 92 parts of 60–80 mesh aqua regia washed Chromosorb-P. This was mounted in a Burrell K-3 Gas Chromatograph.

With this column, the 4- and 7-trimethylsiloxyindenes could be separated, but the 5- and 6-trimethylsiloxyindenes peaks overlapped.

Gas-liquid chromatography of 4- and 7-indenol. The free 4- and 7-indenols were separated on a 20 ft long × $\frac{3}{16}$ in I.D. column of Cu tubing packed with 10% lanolin on 60–80 mesh Chromosorb-W. Column temp was 145°, injection port temp 325°, and the inlet press. of He carrier gas was 90 psi gauge. While separation of the two peaks was not complete, careful freezeout of samples from repetitive injections allowed the collection of several hundred milligrams of each component. The freezeout samples were purified by vacuum sublimation before spectral examination.

Peak #1 (7-indenol). λ 2493 Å (ε 8690), 2820 (sh), 2884 (1843), 2993 (2116); 3·07 μ (s), 5·20 (w), 5·45 (w), 5·72 (w), 6·13 (m), 6·25 (m), 6·41 (m), 6·83 (s), 7·16 (w), 7·29 (w), 7·41–7·46 (m), 7·59 (m), 7·96 (s), 8·21 (w), 8·65 (m), 9·18 (m), 9·48 (w), 9·94 (s), 10·08 (m), 10·93 (m), 12·00 (w), 12·18 (m), 12·68–12·85 (s), 13·88 (w), 14·21–14·33 (s), 15·27 (w).

M.p. 75·0–77·5°, α-naphthylurethan, m.p. 166·0–166·5°.

Peak #2 (4-indenol). λ 2506 Å (ε 7935), 2600 (sh), 2944 (2550), 3052 (2587); 3·17 μ (s), 5·23 (w), 5·45 (w), 5·70 (w), 6·16 (w), 6·26 (m), 6·43 (w), 6·79 (m), 6·88 (m), 7·23 (m), 7·48 (m), 7·70 (w), 7·90 (w), 8·20 (s), 8·59 (m), 8·93 (w), 9·08 (w), 9·53 (m), 10·23 (s), 10·59 (m), 10·94 (m), 11·40 (m), 11·69 (m), 12·27 (w), 13·05 (m), 13·41 (s), 14·50 (m).

M.p. 79·0–82·0°; α-naphthylurethan, m.p. 156·0–156·5°.

Thermal isomerization of 4- and 7-indenols. Freezeouts of 4-indenol from the preceding separation were dissolved in benzene and reinjected into the same apparatus at varying injection port temp. As the temp was increased from 185° to 310°, the ratio of the 4-indenol peak to the 7-indenol peak decreased, and approached an equilibrium ratio. Similar results were observed starting with 7-indenol, which isomerizes to a mixture of 4- and 7-indenol. Here, too, the ratio of peak heights changed with increasing injection port temp, approaching the same equilibrium value.

Isomerization of both 4- and 7-trimethylsiloxyindene to an equilibrium mixture was carried out similarly on the capillary column. In this case, an estimate of the surface temp of the cartridge heater inside the injection port was obtained by means of a thermocouple. This is shown in Fig. 1.

Base catalyzed isomerization of 4- and 7-indenol. A 0·5 M solution of either 4- or 7-indenol in pyridine was treated with one drop of freshly distilled (from KOH) triethylamine at room temp. Samples of the resulting solution were chromatographed on a 12 ft × $\frac{1}{8}$ in I.D. coiled column packed with 10% lanolin on 60–80 mesh Chromosorb-W, with column temp of 160° and injection port at 180°. Samples taken at different times showed progressive isomerization to an equilibrium ratio. Isomerization appeared complete in about 2½ hr.

Pyridine solutions of the indenols remained unchanged during a 2 hr period.

Treatment of 7-indenol with *p*-toluenesulfonic acid in benzene showed no observable isomerization. Extensive polymerization was observed.

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