

INDENOLS IN COAL TARS. THE FIRST PREPARATION OF INDENOL.

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Indenes have long been known to be major constituents of coal tar, but only recently evidence for the presence of indenols has come from examination of several coal tars by low ionizing voltage mass spectrometry.^{1/} This evidence is based on the appearance of a series of peaks at mass units corresponding to the molecular weights of indenol and its homologues in coal tar phenolic fractions. This series of peaks parallels the corresponding indanol series of mass unit peaks. These ubiquitous but elusive compounds may be responsible for much of the gum formation in coal tar, particularly in the tar acid fraction.

The parent hydrocarbon, indene, has been a chemical of commerce for several years, and recently a series of indene derivatives has been made available for development purposes. The commercial importance of these compounds stems from their high chemical reactivity. In the case of indenols, which appear to be major components of certain coal tars, the presence of a phenolic group as well as an olefinic bond in conjugation with an aromatic ring would be expected to provide even greater opportunity for reaction.

While indene and several of its derivatives are thus readily available, indenols have escaped both synthesis and isolation. Two derivatives of indenol, an indenol-O-acetic acid^{2/} and a methoxyindene^{3/} have been reported in the literature, but no reference exists for any preparation of the parent phenol. It should be pointed out that 1-indenol is known, but this compound is not phenolic.

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

We have now developed a successful procedure for preparing both 4- and 5-indenol by catalytic dehydrogenation of the respective indanols which are available from coal tar. Initially, a procedure developed by Webb and Corson^{4/} for the dehydrogenation of substituted ethylbenzenes to the corresponding styrenes was adapted. The method involves passing steam and indanol over a chromia-alumina catalyst at 570° C. The procedure was not always 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 have been developed for purifying the product. In the dehydrogenation itself, nitrogen has been substituted for steam as a carrier gas. The pyrolysis temperature has been increased to 650° C. In this way, we have succeeded in preparing sizeable quantities of indenols in good yields from both 4- and 5-indanol. The same procedure has been used to dehydrogenate indanol trimethylsilyl ethers to the corresponding indenol trimethylsilyl

ethers. 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 product and appear to be more stable during storage. 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 non-polar nature of the ethers is an additional advantage, allowing a wider choice of column packing and giving better separation and less tailing of peaks.

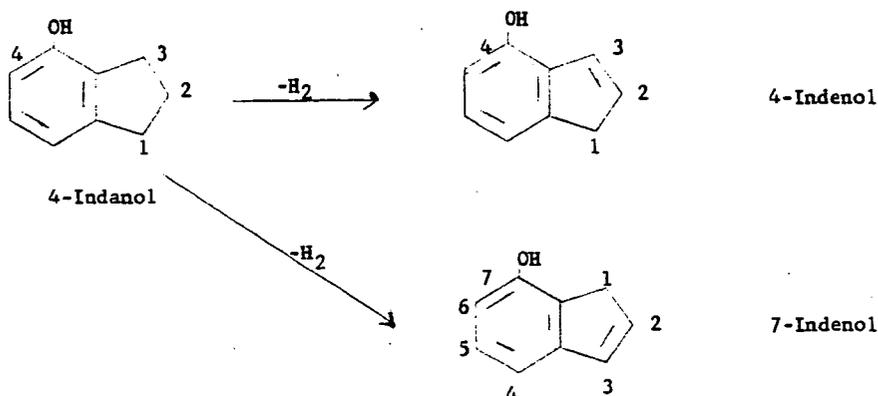
Both the indanol and indenol trimethylsilyl ethers are readily prepared by refluxing the phenols with hexamethyldisilazane,^{5/} and the indenols are easily regenerated from the ethers by refluxing with ethanol.

The initial isolations of pure indenols required repeated recrystallizations from petroleum ether to obtain pure, 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).

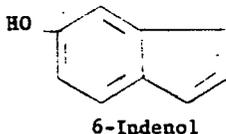
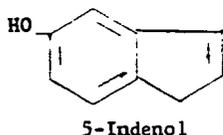
Subsequently, several chromatographic procedures were developed which allowed cleaner separation of indenol from indanol. The first chromatographic separation was carried out using a glass column packed with Chromosorb on which was adsorbed aqueous AgNO_3 solution.^{6,7/} Crude indanol-indenol pyrolyzate mixtures were dissolved in heptane and put on the column. Elution with more heptane removed only indanol. The indenol was eluted with methyl isobutyl ketone.

The second, more efficient chromatographic separation was a similar procedure, called "ligand exchange."^{8/} This procedure combines ion exchange and coordination chemistry to accomplish a task that neither could do alone. An ion exchange is prepared from an ion exchanger resin and a suitable metal ion (in this case Ag^+) which can complex with the appropriate ligand (in this case an olefin). In the procedure used, a Dowex cation exchanger resin was washed with an aqueous solution of silver nitrate and then air-dried. The silver impregnated resin was packed into a chromatographic column and an indanol-indenol mixture in acetone 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 pure (99+ percent) indenol in the chloroform eluate. This proved to be the best way to obtain analytically pure indenol samples.

The initial gas chromatographic analysis of the indenols was used to determine ratios of indanol to indenol in pyrolyzate products and later in purified material. It was evident at an early stage of this problem that dehydrogenation of an indanol did not produce a single product, since the indenol peak on a gas chromatogram was readily resolved in each case into two peaks. The dehydrogenation product from 4-indanol was separated on a column to give two different peaks, which have the same mass and almost identical ultraviolet spectra. It is believed that these two compounds are the isomers, 4- and 7-indenol, both of which can be formed by dehydrogenation of 4-indanol.



The ease with which these two compounds isomerize is not known. However, the individual isomers appear to be stable with respect to each other, since freezing out a given isomer and re-injection in the column fails to show any evidence of isomerization of the given material. This isomeric pair phenomenon also has been found in the product of dehydrogenation of 5-indanol. The 5- and 6-indenol so produced are less readily separated by gas chromatography (Figure 1).



Ingold,^{3/} in his investigation of the 5-(6-) methoxyindenes, came to the conclusion that the material behaved as though it were a mixture of the two isomers. Wheland^{9/} has referred to the compounds as tautomers. However, this is based on observations of experiments which could have given rise to isomerization. Whether true tautomerism exists has yet to be demonstrated. In fact, the gas chromatographic behavior reported here implies a stability great enough to deny the title of tautomers to these pairs of isomers.

Various spectral techniques have been applied to this problem to verify the structure of the indenols. The nuclear magnetic resonance spectra of both indenol samples is consistent with the proposed formulas in that there are two olefinic hydrogens having the same chemical shift as those in indene.^{10/} Ultraviolet spectra of the indenols and their trimethylsilyl ethers bear the same relationship to the spectrum of indene as do those of the indanols and their trimethylsilyl ethers to the spectrum of indane. The infrared spectra of the samples are consistent with indenol structures.

EXPERIMENTAL

The 4- and 5-indanols used in this work have been obtained from Aldrich Chemical Co. and Rutgerswerke A. G. (Germany).

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 feet of #20 B&S nichrome wire covered with porcelain insulator beads. The furnace portion

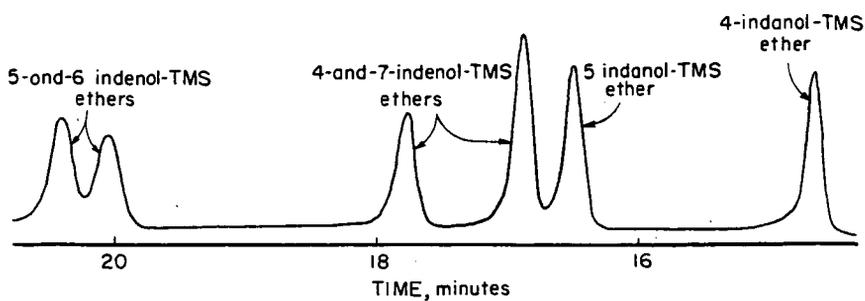


Figure 1.—Gas chromatography on a capillary column of a mixture of trimethylsilyl ethers of indanols and indenols

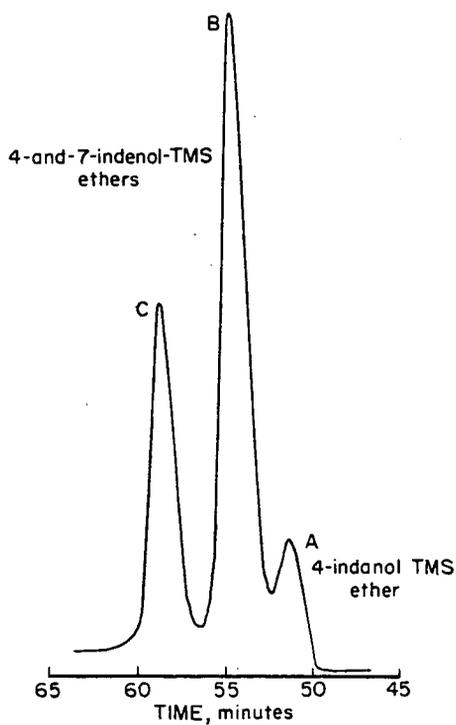


Figure 2.—Gas chromatography on a packed column of indanol-indenol mixture, as trimethylsilyl ethers.

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 nitrogen. 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 Catalyst

A solution of 225 grams of ammonium dichromate and 450 grams of aluminum nitrate nonahydrate in 1500 milliliters of distilled water was warmed to 80° C. Ammonium hydroxide was added until precipitation was complete. The precipitate was filtered and dried at 110° C and then decomposed at 500° C. The powder was pelleted with 4 percent aluminum stearate to 1/8-inch diameter pellets. The catalyst was activated by heating to 570° in a stream of air.

Preparation of 4-Trimethylsiloxyindane

A solution of 20 grams of 4-indanol in 30 milliliters of hexamethyldisilazane was refluxed overnight under nitrogen. The excess hexamethyldisilazane was removed by distillation and the trimethylsilyl ether distilled under vacuum (bp 86-88 at 5 mm.).

Dehydrogenation of 4-Trimethylsiloxyindane

While a stream of nitrogen was flowing through the pyrolysis column, 30 grams of 4-trimethylsiloxyindane was allowed to drip onto the column at a rate of 30 grams per hour. The column temperature was kept at 650° C. The product was collected in three traps, the first of which was cooled in acetone/dry ice and the other two, which contained a mixture of benzene and petroleum ether, were cooled in ice water. The solvent was evaporated from the combined trap contents to yield over 25 grams of 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 indenol trimethylsilyl ether was refluxed overnight in ethanol to hydrolyze it to the indenol. The indenol was recrystallized from carbon tetrachloride and from petroleum ether to give needles, mp 77.5-79° C. Calcd. C_9H_8O : C, 81.79; H, 6.10. Found: C, 82.07; H, 6.46.

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.

Dehydrogenation of 5-Trimethylsiloxyindane

In a similar manner, a mixture of 5- and 6-trimethylsiloxyindane, having a gas chromatographic peak ratio of 4 to 3, was prepared by dehydrogenation of 5-trimethylsiloxyindane (bp 97-99 at 6-7 mm.). The material was converted by refluxing in ethanol to the indenol, mp 78-79.5° C. Calcd. for C_9H_8O : C, 81.79; H, 6.10. Found: C, 81.92; H, 6.20.

Dehydrogenation of 5-Indanol

While a stream of nitrogen was flowing through the pyrolysis column, molten 5-indanol was dripped onto the column at a rate of 30 grams per hour with the column temperature at 650° C. 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.

Figure 1 is a chromatogram of a synthetic indanol-indenol-TMS ether mixture run on a 150-foot x 0.01-inch I.D. capillary column coated with Ucon LB-550-X (a polyalkylene glycol containing an oxidation inhibitor). This capillary column is mounted in a Perkin-Elmer 154 Gas Chromatograph equipped with a hydrogen-flame ionization detector.

The compounds shown in Figure 1, in order of emergence, are: 4-indanol-TMS ether, 5-indanol-TMS ether, 4- and 7-indenol-TMS ethers, and 5- and 6-indenol-TMS ethers. Previous work on a 20-foot by 1/8-inch packed column containing DC 550 silicone oil showed that the 4- and 7-indenol-TMS ethers could be separated, but not the 5- and 6-indenol-TMS ethers.

The conditions used to obtain the results shown in Figure 1 were: column temperature, 151° C; flash vaporizer temperature, 212° C; inlet pressure of N₂ carrier gas, 17.9 psi gauge.

In addition, larger samples were run on a column made from a piece of copper tubing, 610 cm. x 0.30 cm. I. D., coiled as a helix, and containing 12.4 grams of packing, made up in the weight ratio of 8 parts of D.C. 550 silicone oil to 92 parts of 60-80 mesh aqua regia washed Chromosorb. This was mounted in a Burrell K-3 Gas Chromatograph.

Figure 2 is a chromatogram of an indanol-indenol trimethylsilyl (TMS) ether mixture obtained by liquid-liquid chromatography run on this 20-foot silicone column. On the basis of relative retention-time measurements, peak A in Figure 1 is 4-indanol-TMS ether. Peaks B and C are believed to be the 4- and 7-indenol-TMS ethers.

Liquid-Liquid Chromatography of Indenols

The packings for the liquid chromatography experiments were made by absorbing an aqueous AgNO₃ solution onto dry Chromosorb. The AgNO₃ solution in a polyethylene squeeze bottle was sprayed in small increments onto the Chromosorb (in a flask), which was rotated and mixed between successive additions of the AgNO₃ solution.

The "wet" packing (which is still free-flowing) was then put into a glass column 69-inches long and of 3/4-inch inside diameter for the top 30 inches and 1/2-inch inside diameter for the bottom 39 inches. The glass column was jacketed to allow for passing cooling water or refrigerant around the chromatographic column.

The liquid-liquid chromatographic separation on an indanol-indenol mixture was made using a packing which contained 46.3 grams of AgNO₃ solution (60 grams AgNO₃/100 grams solution) per 110 grams of 80-100 mesh Chromosorb. This "wet" packing, 114.2 grams, was packed into the glass column described above. The sample of 0.60 gram of 4-indanol pyrolyzate (recrystallized from heptane) was dissolved in 40 milliliters of heptane, put onto the column, and eluted with 400 milliliters of heptane. During the run, the column was at room temperature. Selected 12-milliliter fractions (chosen on the basis of their refractive index) of the eluate were combined and evaporated to dryness (35° C maximum temperature). The phenolic residues were converted to their trimethylsilyl ethers, and analyzed by gas chromatography. The only substance eluted from the column was 4-indanol; the indenols were held on the column packing. After the heptane-eluted indanol had come out of the column, methyl isobutyl ketone (MIBK) was used and the indenol was then eluted in the MIBK-containing fractions.

The solvent from the indenol-containing fractions was evaporated off, and the trimethylsilyl ethers prepared from this phenolic mixture. This preparation contained a fine blackish precipitate, which suggests that the indenol was eluted from the column as a silver complex or salt, which was then decomposed during the preparation of the trimethylsilyl ethers, depositing metallic silver.

Preparation of Ion Exchange Column Containing Ag⁺

A chromatographic column was filled with 200 grams of 50-100 mesh Dowex 50-X8 cation exchange resin. An aqueous silver nitrate solution containing 95 grams of silver nitrate was poured through the resin filled column. The resin was washed with water and then air-dried. The silver impregnated resin was packed into the chromatographic column.

Separation of 5-Indanol and 5(6)-Indenol

A mixture containing 2 grams of 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° petroleum ether. Elution was carried out with petroleum ether. Gas chromatographic examination of the eluate showed that only 5-indanol was present. Elution with chloroform 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 chloroform then gave pure indenol.

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