National Research Council does not possess the necessary resolution for sorting the spectra of the 2,4-dinitrophenylhydrazones. A system in which the cards are punched every 0.1 micron, however, is satisfactory.

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Preparation and Properties of Some Methylated Indans

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Analysis of mixtures of methylated indans with polymethylbenzenes requires a knowledge of the methylated indans which heretofore has not been well established. In this work a group of authentic methylated indans have been synthesized and purified; the physical properties, including infrared and ultraviolet spectra, have been measured. The determination of these properties permits definite characterization of methylated indans.

IN RECENT studies on the nuclear structure of the watersoluble polycarboxylic acids from the oxidation of bituminous coals, the esters of the coal acids have been subjected to hydrogenolysis to convert the carbalkoxy groups to methyl groups (18). The resulting methylated compounds have been fractionally distilled in precision columns and the expected di-, tri-, and tetramethylbenzenes have been isolated and definitely characterized. In addition to these polymethylbenzenes, however, other aromatic and saturated hydrocarbons and oxygenated compounds are also present.

A number of the properties of the methylated bicyclic aromatics overlap those of the methylated benzenes. To aid in the characterization of such bicyclic aromatics in mixtures with polymethylbenzenes, information on the properties of the simpler methylated bicyclics is desirable. As infrared spectra have proved to be of great value in the identification of hydrocarbons in mixtures, the primary aim of the work was to obtain such spectra. The present

Table I. Physical Properties of Samples

| | | | | Specific | Molar Refraction | |
|---|--|---|---|--|---|---|
| Sample | Boiling Point, ° C. | $n_{\ \mathrm{D}}^{25}$ | d_4^{25} | Refraction | Obsd. | Calcd. |
| Indene Indan cis-Hexahydroindan 1-Methylindan 2-Methylindan 5-Methylindan 1,2-Dimethylindan 1,3-Dimethylindan 1,6-Dimethylindan | 181.8 at 739.5 mm. 176.7 at 739.2 mm. 167.1 at 739.2 mm. 189.5 at 739.2 mm. 190.3 at 739.2 mm. 205.3 at 740.5 mm. 201.1 at 740.5 mm. 202.3 at 740.5 mm. 210.9 at 740.0 mm. | $\begin{array}{c} 1.5739\\ 1.5355\\ 1.4698\\ 1.5241\\ 1.5193\\ 1.5322\\ 1.5311\\ 1.5170\\ 1.5147\\ 1.5209\end{array}$ | $\begin{array}{c} 0.9949\\ 0.9604\\ 0.8808\\ 0.9384\\ 0.9411\\ 0.9662\\ 0.9442\\ 0.9264\\ 0.9252\\ 0.9289\end{array}$ | $\begin{array}{c} 0.3316\\ 0.3244\\ 0.3166\\ 0.3261\\ 0.3227\\ 0.3208\\ 0.3277\\ 0.3265\\ 0.3258\\ 0.3278\\ \end{array}$ | $\begin{array}{c} 38.52 \\ 38.33 \\ 39.33 \\ 43.11 \\ 42.66 \\ 42.41 \\ 43.32 \\ 47.74 \\ 47.64 \\ 47.93 \end{array}$ | $\begin{array}{r} 37.49\\ 37.96\\ 39.36\\ 42.58\\ 42.58\\ 42.58\\ 42.58\\ 42.58\\ 42.58\\ 47.20\\ 47.20\\ 47.20\\ 47.20\end{array}$ |

paper deals with the preparation and properties of a group of methylated indans. The indans were synthesized by conventional methods, purified by fractional distillation in columns of 50 theoretical plates, and subjected to physical measurements. Physical properties are shown in Table I, ultraviolet spectra in Figure 1, and infrared spectra in Figures 2 to 11. The infrared spectra appear to be a very effective means of identifying methylated indans in mixtures of close-boiling polymethylbenzenes.

PREPARATION OF SAMPLES

Indene, indan, and *cis*-hexahydroindan were samples previously described (θ) .

Seventy-three grams of 3-methyl-1-indanone, 1-Methylindan. prepared as described by Koelsch *et al.* (10), was reduced by the Clemmensen method (12, 13). The yield of 1-methylindan was 34.6 grams or 52.4%.

As outlined by Dox and Yoder (5), 568 2-Methylindan. grams (3.46 moles) of α -methylhydrocinnamic acid was prepared

as follows: Benzyl chloride (632 grams, 5 moles) was added to 847 grams (4.87 moles) of the diethyl ester of methylmalonic acid (14) and 115 grams of sodium in ethanol solution, and the resulting diethyl benzylmethylmalonate (4) was saponified to the dibasic acid, which was then decarboxylated by refluxing at 100 mm. The monobasic acid was converted to 596 grams (3.27 moles) of α -methylhydrocinnamoyl chloride by treating it with 420 ml. of thionyl chloride. In the presence of 600 grams of anhydrous aluminum chloride in 1500 ml. of benzene this acid chloride cyclized to 433 grams (2.97 moles) of 2-methyl-1-(Continued on page 1310)



WAVE LENGTH (mµ) Figure 1. Ultraviolet Spectra in Iso-octane Solution





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indanone (3). This ketone (146 grams or 1 mole) was reduced by the Clemmensen method (12, 17) to 87 grams (0.66 mole) of 2-methylindan.

4-Methylindan. Eighteen grams of 4-methylindan was prepared by the method of Hickenbottom *et al.* (θ) .

5-Methylindan. 5-Chloromethylindan (245 grams, 1.47 moles) was prepared from 360 grams (3.05 moles) of indan by the method described by Arnold (2). It was then reduced catalytically over palladium on charcoal to 150 grams (1.13 moles) of 5-methylindan as described by Plattner and Roniger (16).

1,2-Dimethylindan. Two hundred and four grams of 2-methyl-1-indanone (1.40 moles) (cf. above) was converted to 1,2-dimethyl-1-indanol by reaction with methyl magnesium iodide as described by Plattner and Wyss (17). The tertiary alcohol was dehydrated over activated alumina at 300° C. and the resulting olefin was hydrogenated over palladium on charcoal catalyst to produce 150 grams (1.03 moles) of 1,2-dimethylindan.

1,3-Dimethylindan. As described by Plattner et al. (15), 367 grams (2.51 moles) of 3-methyl-1-indanone was converted to 1,3-dimethyl-1-indanol by reaction with methyl magnesium bromide. The tertiary alcohol was dehydrated over activated alumina at 300° C.; the olefin was hydrogenated over palladium on charcoal catalyst to yield 215 grams (1.47 moles) of 1,3-dimethylindan.

1,6-Dimethylindan. 3,5-Dimethyl-1-indanone was prepared in a manner similar to that of Hart and Tebbe (8). A solution of 327 grams (3.15 moles) of crotonyl chloride, 276 grams (3.0 moles) of toluene, and 375 ml. of carbon disulfide was added over 1 hour to a solution of 480 grams (3.6 moles) of anhydrous aluminum chloride in 1875 ml. of carbon disulfide. After 3 hours of stirring at room temperature, the carbon disulfide was distilled in vacuo. To the oily residue was added 3750 ml. of concentrated sulfuric acid, and the mixture was heated at 90° C. for 45 minutes, then cooled to room temperature and decomposed by pouring over ice. The resulting crude ketone was recovered by exhaustive extraction with ether and subsequent distillation of the ether.

The crude ketone was then reduced by the Clemmensen method (12) and the product was carefully fractionated in several batches in a column of 50 theoretical plates. Fractions with the same ranges of boiling points and refractive indices were combined as follows:

| Fraction | B.P., 740 Mm. (Uncorr.), ° C. | n_{D}^{25} | Grams |
|------------------|---|--|--------------------------------|
| A B C D | 205.0 to 208.0 208.0 208.0 208.0 208.0 to 208.4 | 1.5005 to 1.5206 1.5209 1.5210 1.5213 to 1.5219 | $23.4 \\ 102.5 \\ 8.4 \\ 21.5$ |

Fraction B was proved to be 1,6-dimethylindan by oxidation with alkaline permanganate to trimellitic acid (1,2,4-benzenetricarboxylic acid) which was characterized as its anhydride, melting point 165–167 ° C. (19). The other fractions were not investigated for the presence of 1,4-dimethylindan, which on oxidation would give hemimellitic acid (1,2,3-) and which would appear if the toluene had been alkylated on the ortho as well as the para position. In both cases the methyl group on the "1"-position is established by the method of synthesis from crotonyl chloride.

PROPERTIES OF SAMPLES

Each of the samples was carefully fractionated in a column of 50 theoretical plates; a middle portion of the material of constant boiling point and constant refraction was then used for the measurements of physical properties. In the absence of calorimetric measurements a quantitative estimation of the amount of impurity is uncertain. On the basis of method of synthesis and careful fractionation it is believed that all the samples have a purity of at least 95 mole %. However, the samples of 1,2- and 1,3-dimethylindan may consist of mixtures of both cis and trans forms.

Boiling Points. The boiling points were determined in a semimicro-Cottrell boiling point apparatus constructed as described by Willard and Crabtree (20), except that the thermopile was replaced by a single-junction iron-constant an thermocouple with a Type K Leeds and Northrup potentiometer for e.m.f. measurements. The melting point of standard temperature tin sample 42C, measured with this thermocouple and potentiometer, was found to be 232.0° C.; this sample was certified by the National Bureau of Standards to melt at 231.87° C. The ambient pressures were measured with a Taylor temperature-compensated aneroid barometer.

Densities and Refractive Indices. Densities were determined in a 5.4-ml. Sprengel-Ostwald type pycnometer and refractive indices on a Zeiss Abbe type refractometer No. 37489. In both cases the temperatures were maintained to $\pm 0.2^{\circ}$ C. by a Precision Scientific Co. constant temperature bath and circulating system. The specific refractions were obtained using the Lorentz-Lorenz equation. The molar refractions were calculated from the theoretical values of Auwers and Eisenlohr and show exhaltations expected for aromatic polycyclics (11). Spectra. Absorption spectra were run on the Baird infrared

Spectra. Absorption spectra were run on the Baird infrared and Cary ultraviolet recording spectrophotometers of the Mellon Institute, Pittsburgh, Pa. The term, $\log \epsilon$, used in the ultraviolet spectra, Figure 1, refers to the logarithm of the molar extinction coefficient. The stray energy for the Baird infrared spectrophotometer as determined with a Fluorite plate in the sample beam path was 0% transmittance from 2.0 to 12.0 microns. From 12.0 to 14.15 microns the stray energy rose linearly from 0 to 5% transmittance and from 14.15 to 16.0 microns it increased linearly but with greater slope from 5 to 52% transmittance.

A few of the absorption spectra have appeared elsewhere; among the most notable are those from API Research Project No. 44(1) and those of Felgett *et al.* (7).

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