Part II

PHYSICAL PROPERTIES
EVALUATION OF COMPOUNDS AND MATERIALS

Preparation, Properties, and Spectra of Eight Alkylated Indenes

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IN THE SEPARATION and identification of alkyl aromatic hydrocarbons from the neutral oil of a low-temperature bituminous coal tar, it was found that the required spectra of authentic specimens of alkylindenes were unavailable. The properties and spectra of eight methylated indans have been reported by Entel, Ruof, and Howard (*4, 5*), and have proved to be of great value in the characterization of the neutral oil. Similar information was desired for the alkylated indenes, a characteristic class of aromatic hydrocarbon in low-temperature coal tars, and other oils of pyrolytic origin. In the present project, eight alkylated indenes have been prepared and purified; two of these have not been reported previously. Physical properties, including spectra, have been determined.

EXPERIMENTAL

Preparation of Alkylated Indenes. 2-Methylindene, 2-ethylindene, 2,3-dimethylindene, 2,6-dimethylindene, and 2,3,6-trimethylindene were synthesized from the appropriate alkyl aryl ketone by the procedure of Colonge and Weinstein (*3*). A 50 to 100% excess of the ketone was allowed to react at room temperature for 5 to 7 hours in a potassium hydroxide–95% ethyl alcohol mixture with trioxymethylene as a source of formaldehyde. The resulting 1,3-ketol was then cyclodehydrated with concentrated sulfuric acid to give an indanone, which was either directly reduced to an indanol or alkylated with the appropriate Grignard reagent in order to introduce an alkyl group in the five-membered ring of the resulting indanol. Following the procedure of Nystrom and Brown (*12*), lithium aluminum hydride was chosen as a reducing agent, and the resulting indanol was dehydrated to the corresponding indene by refluxing with 10% oxalic acid solution. Because 2-ethyl-1-indanol was only partially dehydrated by oxalic acid, the stronger dehydrating agent, 2-naphthalenesulfonic acid, was used, following the procedure of Kohler, Tishler, Potter, and Thompson (*9*).

The available alkyl aryl ketones were propiophenone and *n*-butyrophenone. In addition, 4-methylpropiophenone was synthesized for use as a starting material. The procedure described by Noller and Adams (*11*) was used, which involves a Friedel-Crafts reaction of toluene and propionic anhydride in the presence of anhydrous aluminum chloride.

1-Methylindene and 1,3-dimethylindene were prepared from 3-methyl-1-indanone that was synthesized from benzene and crotonic acid in the presence of anhydrous aluminum chloride, by the procedure of Koelsch, Hochmann, and LeClaire (*8*).

3-Ethylindene was prepared from 1-indanone that was synthesized from hydrocinnamoyl chloride in the presence of anhydrous aluminum chloride, by the procedure of Johnson and Glenn (*7*).

1-Methylindene and 2,6-dimethylindene have never been reported in the literature. API Research Project No. 44 (*1*), Table 47a, lists the refractive index and density of what was thought to be 1-methylindene, but an examination of the original literature referred to in the table revealed that this is actually 3-methylindene. The original literature used a

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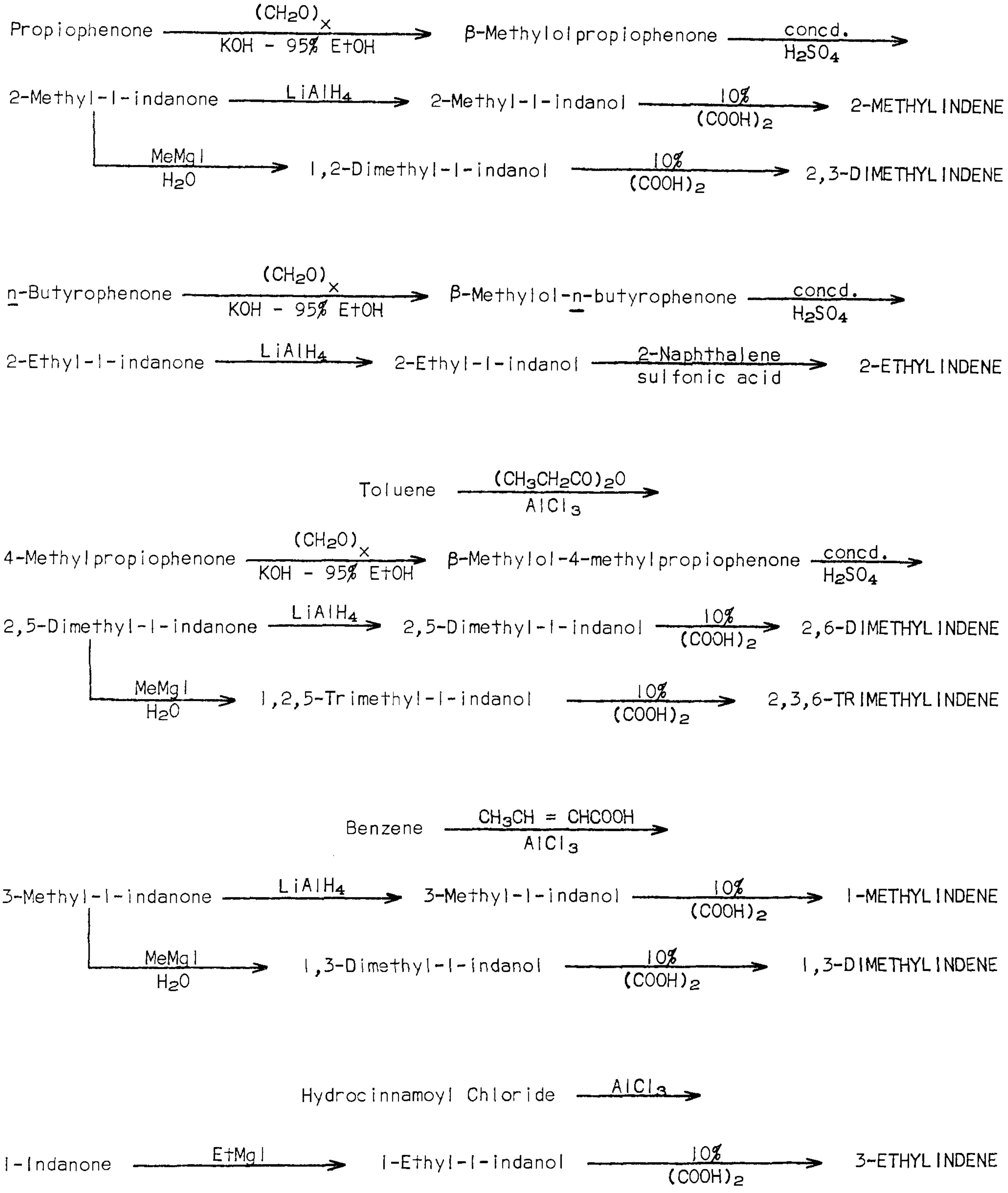

The flow diagram summarizes the preparation of the alkalines

different system of nomenclature—the saturated carbon was the number 3 instead of the number 1 carbon as in the *Chemical Abstracts* system.

The preparation of the alkylindenes is summarized in the flow diagram, which gives the various intermediates.

Table I summarizes the characteristics of the synthesized alkylindenes. The boiling points reported were observed in the reduced pressure fractional distillation equipment used to isolate the alkylindene from the dehydration reaction mixture. The elemental analyses were made on redistilled samples. The hydrogen contents of 2- and 3-ethylindene and 2,6-dimethylindene differed by 0.09 to 0.14 from the theoretical content, indicating the possibility of trace impurities. These compounds were examined for the pres-

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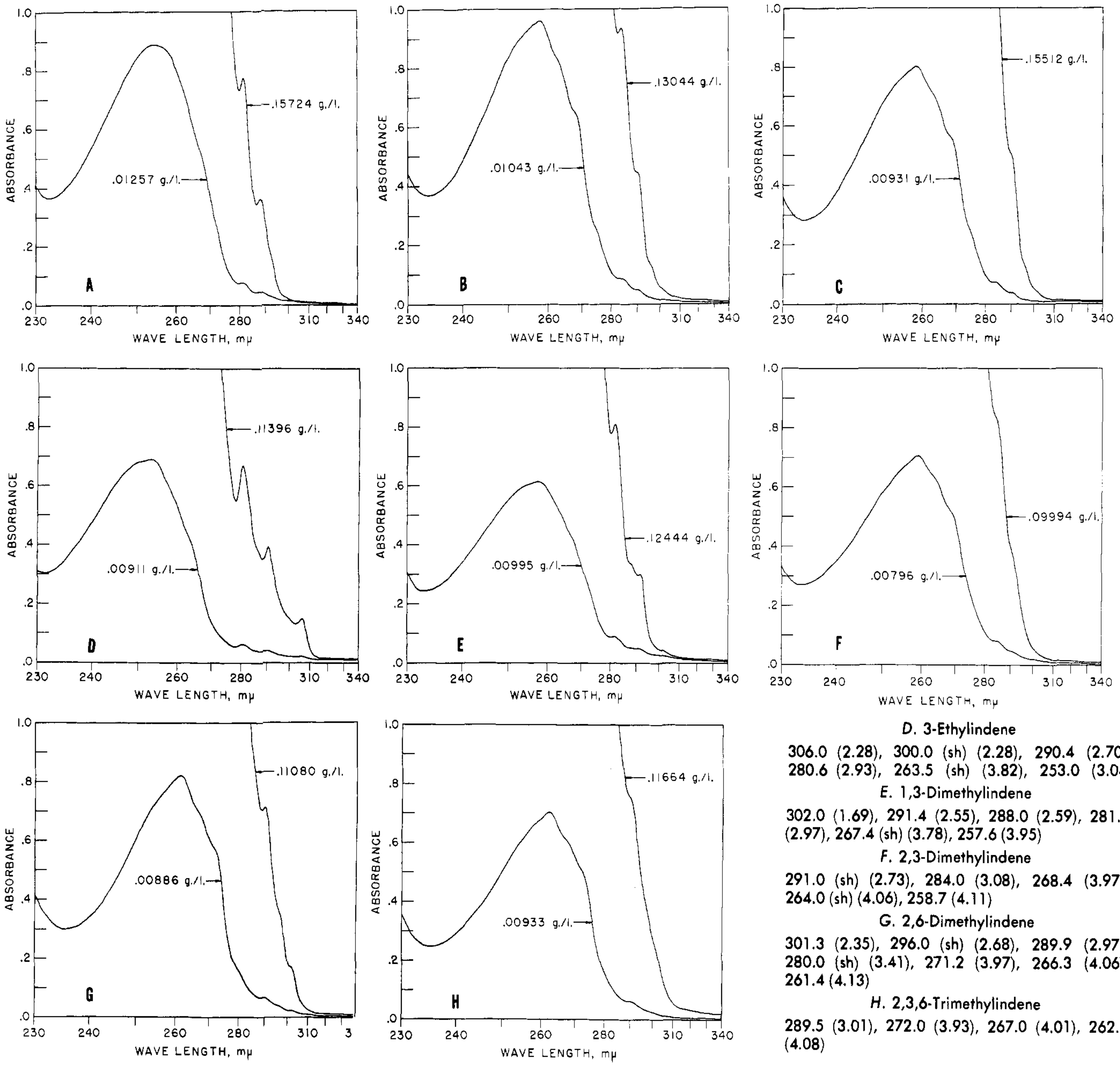


A. 1-Methylindene

292.0 (sh) (2.15), 287.7 (2.48), 281.3 (2.81), 267.0 (sh) (3.73), 254.6 (3.96)

B. 2-Methylindene

296.0 (sh) (2.11), 290.0 (2.65), 283.5 (2.97), 274.0 (sh) (3.52), 267.8 (3.91), 263.0 (sh) (4.01), 257.8 (4.08)

C. 2-Ethylindene

296.0 (sh) (2.05), 289.7 (2.68), 283.7 (3.06), 268.3 (3.94), 263.6 (4.03), 258.4 (4.09)

D. 3-Ethylindene

306.0 (2.28), 300.0 (sh) (2.28), 290.4 (2.70), 280.6 (2.93), 263.5 (sh) (3.82), 253.0 (3.04)

E. 1,3-Dimethylindene

302.0 (1.69), 291.4 (2.55), 288.0 (2.59), 281.5 (2.97), 267.4 (sh) (3.78), 257.6 (3.95)

F. 2,3-Dimethylindene

291.0 (sh) (2.73), 284.0 (3.08), 268.4 (3.97), 264.0 (sh) (4.06), 258.7 (4.11)

G. 2,6-Dimethylindene

301.3 (2.35), 296.0 (sh) (2.68), 289.9 (2.97), 280.0 (sh) (3.41), 271.2 (3.97), 266.3 (4.06), 261.4 (4.13)

H. 2,3,6-Trimethylindene

289.5 (3.01), 272.0 (3.93), 267.0 (4.01), 262.0 (4.08)

Figure 1. Ultraviolet spectra

$\lambda_{max.}^{Cyclohexane}$, mμ (log ε)

Table I. Characteristics of Synthesized Alkyl Indenes

	B.P.		Analysis of Indene, %			
			Calcd.		Found[a]	
Indene	° C.	Mm.	C	H	C	H
1-Methyl-	55-56	3.75	92.26	7.74	92.20	7.75
2-Methyl-	64-65	2.7	92.26	7.74	92.29	7.81
2-Ethyl-	62	1.1	91.61	8.39	91.63	8.50
3-Ethyl-	61-61.5	1.4	91.61	8.39	91.57	8.25
1,3-Dimethyl-	66	3	91.61	8.39	91.41	8.47
2,3-Dimethyl-	77	3	91.61	8.39	91.61	8.37
2,6-Dimethyl-	77	2.5	91.61	8.39	91.66	8.48
2,3,6-Trimethyl-	97	3	91.08	8.92	91.17	8.91

[a] Microanalyses by Schwarzkopf Microanalytical Laboratory, 56-19 37th Ave., Woodside 77, N. Y.

Table II. Physical Properties of Some Alkyl Indenes

	B.P.			
Indene	° C.	Mm.	n^{20}_D	d^{20}_4
1-Methyl-	185.9	735.1	1.5565	0.9635
2-Methyl-	204.1[a]	742.2	1.5645[a]	0.9755[a]
2-Ethyl-	222.5	735.1	1.5598[b]	0.9636[b]
3-Ethyl-	218.1[c]	742.2	1.5572[d]	0.9689[d]
1,3-Dimethyl-	207.5[e]	742.2	1.5477[f]	0.9530[e]
2,3-Dimethyl-	224.5	735.1	1.5612	0.9711
2,6-Dimethyl-	226.8	735.1	1.55815	0.9593
2,3,6-Trimethyl-	242.6	735.1	1.5532[g]	0.9642[g]

[a] API Research Project 44 (*1*) gives b.p. 208° C. at 760 mm., n^{20}_D 1.5652, d^{20}_4 0.9770. [b] Ruzicka and Peyer (*14*) give n^{22}_D 1.5525, d^{22}_4 0.9619. [c] Wislicenus and Hentrich (*15*) give b.p. 215-16° C. at 1 atm. [d] Ruzicka and Peyer (*14*) give n^{22}_D 1.5543, d^{22}_4 0.9645. [e] Braun and Kirschbaum (*2*) give b.p. 212-14° C. at 1 atm., d^{20}_4 0.9553. [f] Plattner, Fürst, and Studer (*13*) give n^{16}_D 1.5509. [g] Colonge and Weinstein (*3*) give n^{24}_D 1.5566, d^{24}_4 0.954.

Figure 2. Infrared spectra

$\lambda_{\max.}^{CS_2}$, μ(Intensity)

A. 1-Methylindene

14.08(s), 13.76(s), 13.55(s), 13.11(s), 12.64(s), 11.57(m), 11.07(m), 10.72(m), 10.02(w), 9.80(m), 9.48(m), 9.36(w), 9.26(w), 8.98(w), 8.68(w), 8.57(w), 8.32(w), 8.15(w), 7.87(w), 7.78(w), 7.60(w), 7.34(m), 7.28(m)

B. 2-Methylindene

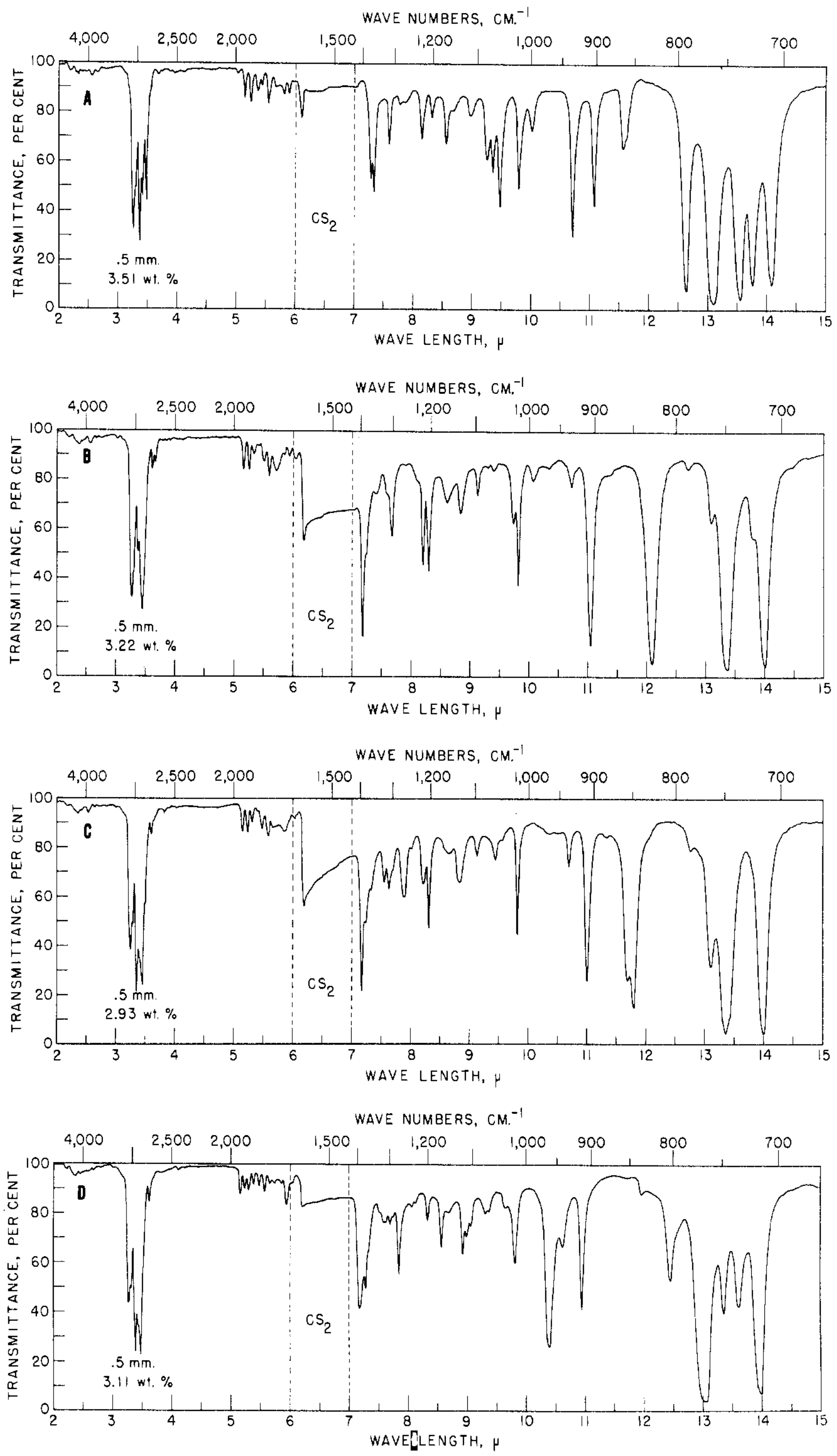
14.00(s), 13.80(w), 13.37(s), 13.10(w), 12.70(w), 12.09(s), 11.04(s), 10.72(w), 10.32(w), 10.07(w), 9.81(m), 9.74(w), 9.40(w), 9.30(w), 9.12(w), 8.84(w), 8.60(w), 8.30(m), 8.20(m), 7.67(w), 7.40(w), 7.24(w), 7.17(m)

C. 2-Ethylindene

14.00(s), 13.35(s), 13.10(m), 12.75(w), 11.79(s), 11.68(w), 11.32(w), 11.00(m), 10.68(w), 9.81(m), 9.55(w), 9.44(w), 9.12(w), 8.83(w), 8.64(w), 8.31(m), 8.21(w), 8.01(w), 7.89(w), 7.62(w), 7.54(w), 7.32(w), 7.24(w), 7.17(m)

D. 3-Ethylindene

13.98(s), 13.62(m), 13.37(m), 13.04(s), 12.45(m), 11.97(w), 10.95(m), 10.63(w) 10.39(s), 9.81(w), 9.65(w), 9.38(w), 9.31(w), 9.07(w), 9.00(w), 8.93(w), 8.70(w), 8.56(w), 8.33(w), 8.13(w), 8.07(w), 7.85(w), 7.75(w), 7.70(w), 7.60(w), 7.53(w), 7.28(w), 7.18(m)



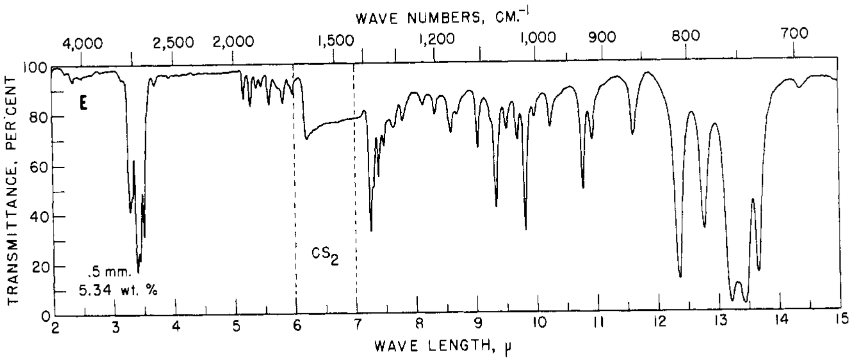
ence of extraneous material by gas-liquid chromatography, by using a column with an efficiency of about 4000 theoretical plates. No extra peaks could be seen on the chromatogram. Upon standing for several months some of the indenes, in particular 1-methylindene, showed extra peaks, indicating a significant amount of autodecomposition of an unknown nature.

Properties and Spectra of Alkylated Indenes. The properties and spectra were determined on the freshly prepared and redistilled samples. Standard techniques were used for the determination of normal boiling point, refractive index, density, and ultraviolet and infrared spectra. The boiling points at atmospheric pressure were determined by the micromethod of Siwoloboff as described by Morton (*10*). This method was throughly checked and calibrated with standard samples having boiling points in the same range as the alkylindenes. The maximum deviation from true values was less than 1°. We intend to publish a detailed description of our improved Siwoloboff micro boiling point method. The refractive indices were determined at 20° C. with an Abbé AO Spencer refractometer, using a sodium vapor lamp as the light source. The densities were determined to within a maximum deviation of ±0.0015 by using microcapillary pycnometers with fourth decimal place scales that had been calibrated with water. These three physical properties for the eight alkylated indenes are summarized in Table II.

The ultraviolet spectra (Figure 1) were obtained on cyclohexane solutions in 1-cm. silica cells with a Beckman DK-2 recording spectrophotometer, and the infrared spectra (Figures 2 and 3) were obtained on carbon disulfide solutions in 0.5-mm. sodium chloride cells with a Model 21

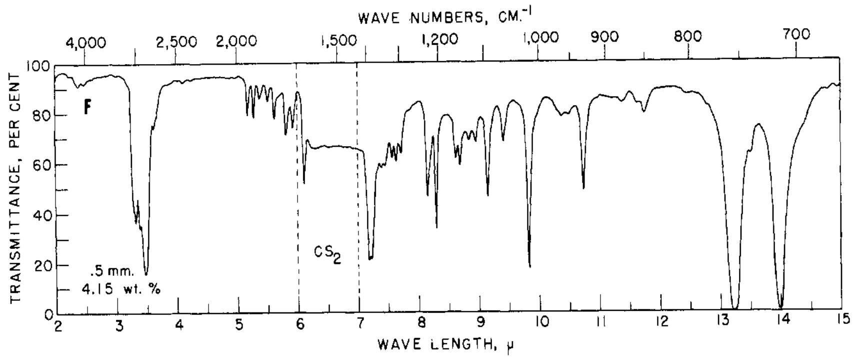
Figure 3. Infrared spectra

$\lambda_{max.}^{CS_2}$, μ (Intensity)



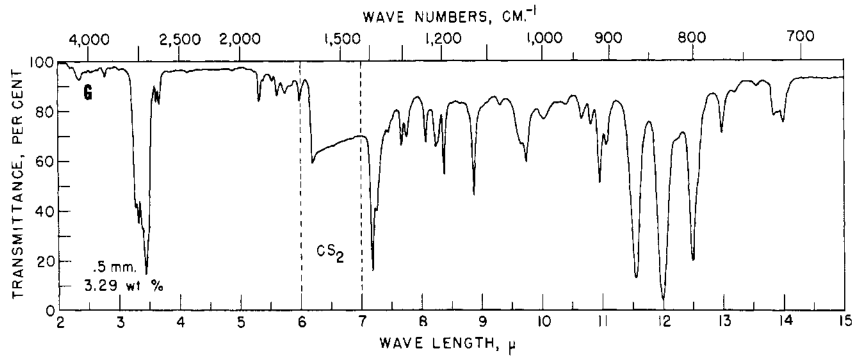
E. 1,3-Dimethylindene

14.37(w), 13.66(s), 13.44(s), 13.22(s), 12.77(m), 12.36(s), 11.60(w), 10.92(w), 10.77(m), 10.23(w), 9.97(w), 9.82(m), 9.69(w), 9.51(w), 9.33(m), 9.25(w), 9.03(w), 8.69(w), 8.58(w), 8.32(w), 8.12(w), 7.80(w), 7.64(w), 7.48(w), 7.39(w), 7.30(w), 7.26(m)



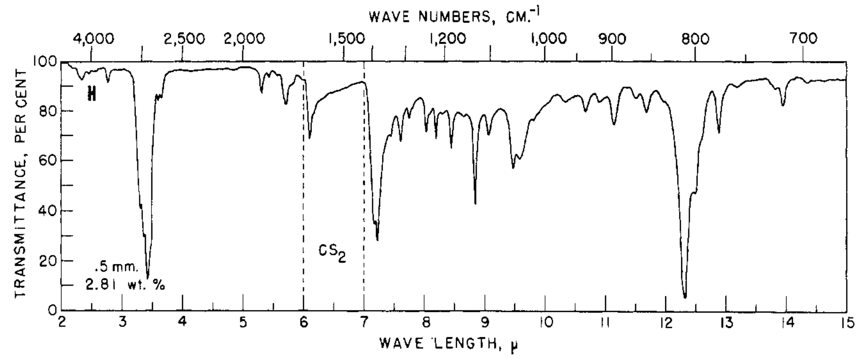
F. 2,3-Dimethylindene

13.97(s), 13.51(w), 13.23(s), 11.75(w), 11.62(w), 11.37(w), 10.74(m), 10.50(w), 10.37(w), 9.83(m), 9.42(w), 9.15(m), 8.96(w), 8.84(w), 8.69(w), 8.62(w), 8.30(m), 8.15(m), 7.72(w), 7.63(w), 7.56(w), 7.45(w), 7.38(w), 7.23(m), 7.18(m)



G. 2,6-Dimethylindene

13.99(w), 13.83(w), 13.53(w), 13.18(w), 12.97(w), 12.48(s), 11.99(s), 11.55(s), 11.06(w), 10.95(m), 10.80(w), 10.65(w), 10.40(w), 10.02(w), 9.74(w), 9.65(w), 9.30(w), 8.87(m), 8.37(m), 8.24(w), 8.07(w), 7.75(w), 7.67(w), 7.45(w), 7.26(w), 7.18(m)



H. 2,3,6-Trimethylindene

13.95(w), 12.88(w), 12.48(w), 12.32(s), 11.68(w), 11.55(w), 11.14(w), 10.90(w), 10.66(w), 10.32(w), 9.80(w), 9.57(w), 9.47(w), 9.07(w), 8.84(m), 8.65(w), 8.44(w), 8.31(w), 8.19(w), 8.03(w), 7.75(w), 7.62(w), 7.44(w), 7.22(m), 7.17(m)

Perkin-Elmer recording spectrophotometer with sodium chloride optics. None of these 16 spectra have been reported previously in the literature. The only previous published spectra of an alkylindene are the ultraviolet (*6*) and infrared (*1*) spectra of 3-methylindene.

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