[Contribution from the Research Department, Standard Oil Company (Indiana)]

Disproportionation of Alkylbenzenes. III. Spectral Characteristics and Other Physical Properties of Symmetrical Trialkylbenzenes. Proof of Structure of 1,3,5-Tri-*t*-butylbenzene[1]

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Nine symmetrical trialkylbenzenes of good purity have been prepared by HF–BF_3 catalysis. The infrared and ultraviolet bands of these compounds show an orderly displacement with changes in the alkyl groups. The boiling point and specific refraction have been related to carbon number. These correlations, along with a molecular weight determined by the mass spectrometer, help to prove the structure of a new compound, 1,3,5-tri-*t*-butylbenzene.

Symmetrical trialkylbenzenes, uncontaminated by other isomers, can be prepared by isomerization or disproportionation with hydrogen fluoride plus boron trifluoride.[2,3] This technique has been used to prepare nine 1,3,5-trialkylbenzenes of sufficiently high purity for a study of their infrared and ultraviolet absorption spectra and other physical properties. Three of these trialkylbenzenes were new compounds. One was a white solid made by the disproportionation of *t*-butylbenzene and believed to be 1,3,5-tri-*t*-butylbenzene.[3] Because previous attempts to prepare tri-*t*-butylbenzenes with an acid catalyst were unsuccessful,[4] a proof of structure, based on spectral evidence,[5] was worked out. A correlation of the spectral properties of the other known symmetrical trialkylbenzenes was essential in this proof of structure. This correlation may be useful in assigning configuration to other unknown hydrocarbons.

Table I

Physical Properties of Symmetrical Trialkylbenzenes

	M.p., °C. Obsd.	M.p., °C. Lit.[14]	B.p., °C. Obsd.	B.p., °C. Lit.[14]	Refractive index $n^{20}D$ Obsd.	Refractive index $n^{20}D$ Lit.[14]	Density, g /ml. at 20° Obsd.	Density, g /ml. at 20° Lit.[14]	Purity, mole % (from freezing points)
1,3-Dimethyl-5-isopropylbenzene	−57.2	−55.3	195.5	191	1.4948	1.4955	0.8600	0.859	99.0–99.5
1,3-Dimethyl-5-*t*-butylbenzene	−18.3	−21.5	209	206	1.4956	1.4958	.8652	.8645	....
1,3,5-Triethylbenzene	−67.1	−66.5	217.5	215.9	1.4958	1.4958	.8633	.8621	99.0–99.5
1,3-Diisopropyl-5-methylbenzene	−60.8	....	217.5	218	1.4910	1.4955	.8572	.8668	99.0–99.5
1,3-Di-*t*-butyl-5-methylbenzene	31.1	32	244	244	1.4900[a]	1.487	.8600[a]	.858	....
1,3,5-Triisopropylbenzene	− 7.4	−15	238	238	1.4882	1.4882	.8545	.8547	99.0–99.5
1,3,5-Tri-*n*-butylbenzene	....	....	315	...	1.4870	....	.8539	....	....
1,3,5-Tri-*sec*-butylbenzene	....	....	284	...	1.4820	....	.8479	....	....
1,3,5-Tri-*t*-butylbenzene	73.3	....	248	...	1.482[b]	....	.853[b]	....	99.5+

[a] Supercooled liquid. [b] Calculated from value in benzene solution.

Experimental

Nine 1,3,5-trialkylbenzenes were prepared by disproportionation of alkylbenzenes in the presence of HF–BF_3.[2,3] The crude 1,3,5-trialkylbenzenes, containing no detectable isomeric material, were fractionated at atmospheric pressure in a 125-plate miniature Hyper-Cal column. A middle portion, containing about 80% of each distillate, was taken for study. The physical properties of the six previously known compounds are compared with literature values in Table I. The median distillation temperature, corrected to 760 mm., was chosen as the boiling point. Refractive indices were measured at 20° on an Abbe refractometer. Densities were determined at 20° with a 3-ml. pycnometer. Melting points and purities were determined cryoscopically.[6]

Additional tests were made on the new compound. A carbon–hydrogen analysis gave: C, 87.90; H, 12.45. Calcd. for $C_{18}H_{30}$: C, 87.73; H, 12.27. A mass spectrum was obtained with a Consolidated Model 21-102 mass spectrometer.

Infrared spectra discussed in this paper were obtained on a Beckman IR2 spectrometer.[7] The Beckman instrument, equipped with a sodium chloride prism, was used to cover the range of 5000 to 670 cm.$^{-1}$. The slit was automatically adjusted by a Servo slit mechanism. To minimize absorption due to atmospheric water vapor, the instrument was continuously flushed with air dried over silica gel. The band positions are accurate to within 1 cm.$^{-1}$ between 1000 and 670 cm.$^{-1}$.

Ultraviolet spectra were measured from 2150 to 3500 Å. on a Beckman DU quartz spectrometer. Some additional spectra were obtained on a Cary recording spectrometer to confirm the reality of weak absorption maxima.

Correlation of Spectra.—The important infrared and ultraviolet absorption bands for each of the trialkylbenzenes prepared are summarized in Figs. 1 and 2.[8] The published spectra[9] of two additional compounds, 1,3,5-trimethylbenzene and 1,3-dimethyl-5-ethylbenzene, are included. Figure 1

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[1] Presented before the Division of Petroleum Chemistry at the 124th Meeting of the American Chemical Society, Chicago, Illinois, September, 1953.

[2] (a) D. A. McCaulay and A. P. Lien, This Journal, **74**, 6246 (1952); (b) A. P. Lien and D. A. McCaulay, *ibid.*, **75**, 2407 (1953).

[3] D. A. McCaulay and A. P. Lien, *ibid.*, **75**, 2411 (1953).

[4] D. I. Legge, *ibid.*, **69**, 2079 (1947).

[5] We have learned from Prof. P. D. Bartlett that he, also, has isolated 1,3,5-tri-*t*-butylbenzene. His proof of structure, based on chemical evidence, is given in This Journal, **76**, 2349 (1954).

[6] A. R. Glasgow, Jr., A. J. Streiff and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 355 (1945).

[7] Additional measurements were made with a Perkin–Elmer 12C spectrometer. Prisms of calcium fluoride (for higher resolution in the region between 5000 and 1250 cm.$^{-1}$) and potassium bromide (to cover the region from 710 to 400 cm.$^{-1}$) were used.

[8] The complete infrared and ultraviolet spectra of these compounds will appear in the Catalogs of Infrared and Ultraviolet Spectral Data of American Petroleum Institute Research Project 44.

[9] Catalog of Infrared Spectral Data, American Petroleum Institute Research Project 44, serial numbers 354 and 737; Ultraviolet, serial numbers 164 and 206.

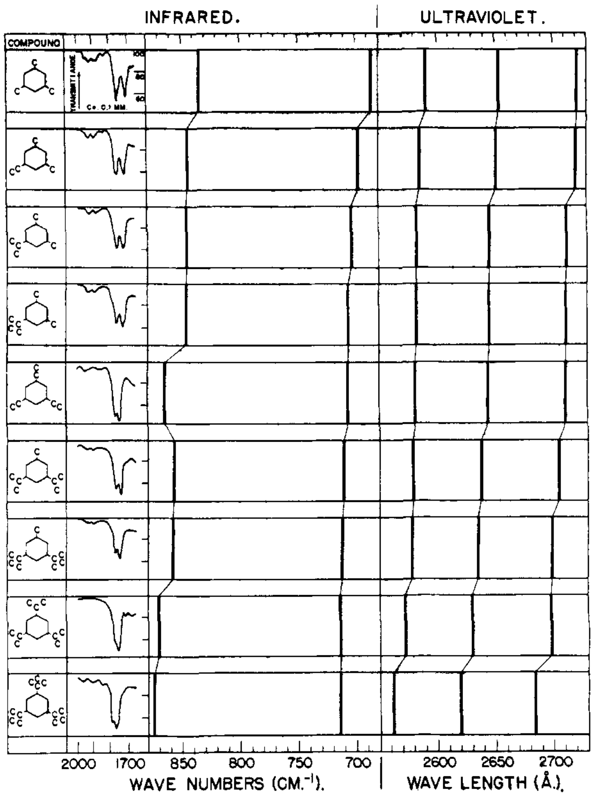

Fig. 1.—Significant absorption bands of methyl derivatives of 1,3,5-trimethylbenzene.

shows the key bands of symmetrical trialkylbenzenes derived from 1,3,5-trimethylbenzene by substitution of methyl groups for hydrogen atoms in the CH_3- side chains. Figure 2 depicts the bands of two symmetrical tri-*n*-alkylbenzenes and two tri-*sec*-alkylbenzenes.

In the infrared region from 1670 to 2000 cm.$^{-1}$ the spectral patterns, made up of overtone and combination frequencies, are characteristic of the number and location of substituent groups on the benzene ring.[10] Each alkylbenzene in Fig. 1 shows the pattern expected of a 1,3,5-substituted ring. This similarity supports the conclusion of Young, DuVall and Wright.[10] The spectral fragments of Fig. 1 suggest a refinement in the correlation: the compounds in which at least two of the substituting groups are methyl groups have patterns that show well-defined doublets; for the other compounds, the high-frequency component of the doublet is weaker or appears as a shoulder.

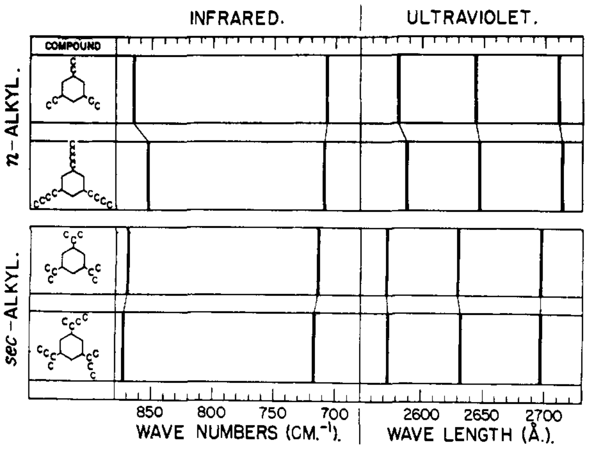

Fig. 2.—Significant absorption bands of 1,3,5-tri-*n*-alkyl- and tri-*sec*-alkylbenzenes.

In the infrared region from 680 to 890 cm.$^{-1}$ absorption frequencies have been correlated with the number and position of substituents on the aromatic ring.[11,12] The previously published spectra of 1,3,5-trimethylbenzene and 1,3-dimethyl-5-ethylbenzene showed two strong bands at about 690 and 840 cm.$^{-1}$ characteristic of 1,3,5-substitution. Similar strong bands appear for the other trialkylbenzenes in Fig. 1, but are gradually displaced to 714 and 874 cm.$^{-1}$, respectively. As the number of carbon atoms increases, the 690 cm.$^{-1}$ band shifts to higher frequencies. The other band, starting at 835 cm.$^{-1}$, also shifts to higher frequencies with each substitution of a methyl group for a hydrogen atom in the CH_3– side chain. The amount of shift, however, depends upon the order of substitution. The first methyl substitution shifts the band 10 units; the second and third substitution in the same CH_3– group each shifts the band 1.5 units. For the trialkylbenzenes of Fig. 1 the band frequency may be calculated from the equation

$$\nu = 835 + 10a + 1.5b$$

where *a* is the number of first substitutions in a methyl group and *b* is the number of second and third substitutions. Table II shows the very close agreement between the observed frequencies and those calculated by the above equation.

TABLE II

OBSERVED AND CALCULATED INFRARED FREQUENCIES

Compound	Obsd. band position, cm.$^{-1}$	Calcd. band position, cm.$^{-1}$
1,3,5-Trimethylbenzene	835	835
1,3-Dimethyl-5-ethylbenzene	845	845
1,3-Dimethyl-5-isopropylbenzene	846	846
1,3-Dimethyl-5-*t*-butylbenzene	847	848
1,3,5-Triethylbenzene	865	865
1,3-Diisopropyl-5-methylbenzene	857	858
1,3-Di-*t*-butyl-5-methylbenzene	858	861
1,3,5-Triisopropylbenzene	870	870
1,3,5-Tri-*t*-butylbenzene	874	874

Figure 2 shows the key absorption bands of two of the three new butylbenzenes: 1,3,5-tri-*n*-butylbenzene and 1,3,5-tri-*sec*-butylbenzene. These two alkylbenzenes are not members of the group of methyl derivatives of 1,3,5-trimethylbenzene, shown in Fig. 1. They are compared in Fig. 2, therefore, with 1,3,5-triethylbenzene and 1,3,5-triisopropylbenzene to show relations between symmetrical tri-*n*-alkylbenzenes and tri-*sec*-alkylbenzenes. Both infrared bands of the tri-*sec*-alkylbenzenes are at higher frequencies than the corresponding bands of the tri-*n*-alkylbenzenes.

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(10) C. W. Young, R. B. DuVall and N. Wright, *Anal. Chem.*, **23**, 709 (1951).

(11) N. B. Colthup, *J. Optical Soc. Am.*, **40**, 397 (1950).

(12) C. G. Cannon and G. B. B. M. Sutherland, *Spectrochim. Acta*, **4**, 373 (1951).

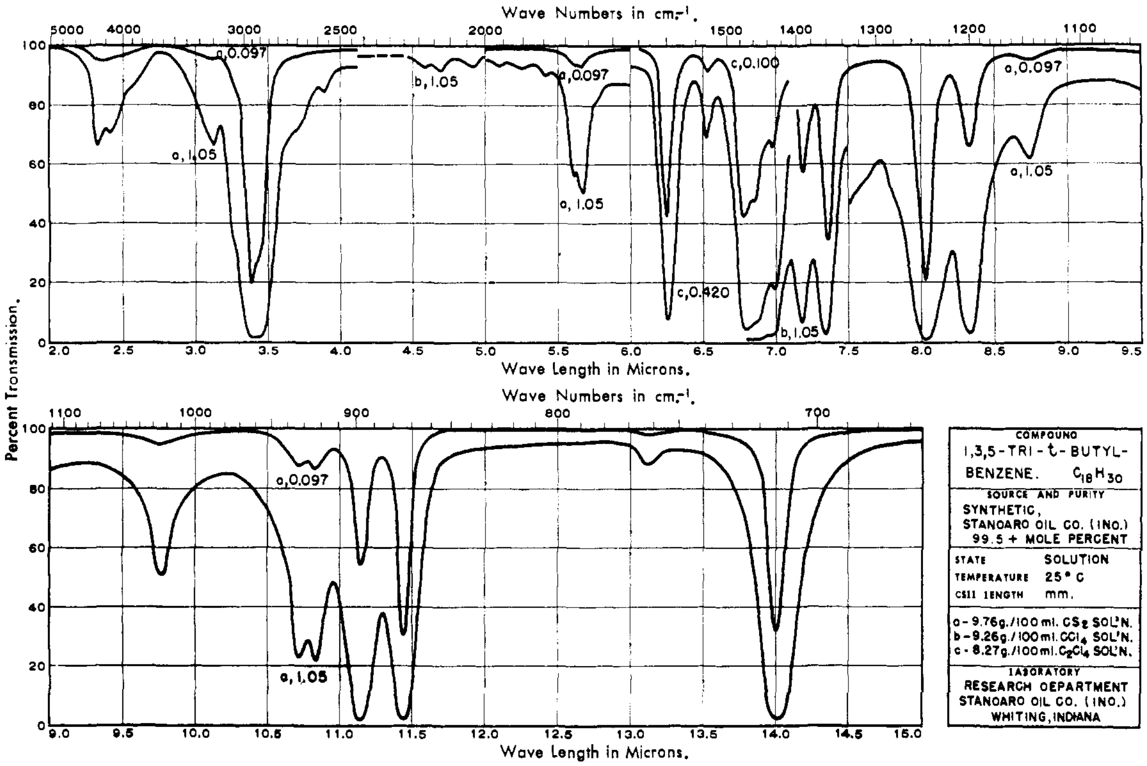

Fig. 3.—Infrared spectrum of tri-*t*-butylbenzene.

In each pair, lengthening the side chain causes the 710 cm.$^{-1}$ band to shift slightly to higher frequencies.

The ultraviolet spectra of all the 1,3,5-trialkylbenzenes show a strong absorption maximum between 2620 and 2653 Å., a well-defined maximum at longer wave length, and a less distinct maximum or shoulder at shorter wave length. These three absorption maxima are depicted in Figs. 1 and 2. For the trialkylbenzenes of Fig. 1, the ultraviolet maxima shift regularly to shorter wave lengths as the number of branches on alpha carbon atoms increases. This sort of shift also appears in Fig. 2, where the ultraviolet bands of the two tri-*sec*-alkylbenzenes are at shorter wave lengths than the corresponding bands of the tri-*n*-alkylbenzenes. In both the *n*-alkyl and *sec*-alkyl pairs, lengthening the side chains causes small bathochromic shifts of the ultraviolet bands.

Proof of Structure of 1,3,5-Tri-*t*-butylbenzene.—An accurate molecular weight determination and the infrared and ultraviolet spectra of 1,3,5-tri-*t*-butylbenzene are used to prove its structure.

Determination of molecular weight by the increase in boiling point of benzene was made difficult by the unexpectedly high volatility of the alkylbenzene. However, this very property made it possible to volatilize the sample into the mass spectrometer. The mass spectrum showed a parent peak at mass number 246; this value, together with the elemental analysis, is consistent with the formula $C_{18}H_{30}$. A stronger peak at 231, corresponds to a fragment derived by the loss of one methyl group, and a strong peak at 57 is due to butyl groups. The remainder of the mass spectrum also is consistent with the structure of 1,3,5-tri-*t*-butylbenzene.

The infrared spectrum of the new compound is given in Fig. 3. The pattern in the region from 1670 to 2000 cm.$^{-1}$ indicates a 1,3,5-substituted ring. The bands at 714 and 874 cm.$^{-1}$, as Figs. 1 and 2 illustrate, not only confirm the 1,3,5-orientation but also suggest that there are at least six branches on the alpha carbons.

Bands at 1200 and 1245 cm.$^{-1}$ are attributable to *t*-butyl groups.[13] Additional evidence for *t*-butyl groups is found in the interval from 1350 to 1400 cm.$^{-1}$, where there are absorption bands due to C–H deformation of methyl groups. Single methyl groups absorb at 1380 cm.$^{-1}$. When two or three methyl groups are attached to the same carbon atom, the 1380 cm.$^{-1}$ band splits into a doublet. For an isopropyl group, the two components are equally strong; for a *t*-butyl group the component of higher frequency is the weaker. Thus, the strong band at 1361 cm.$^{-1}$ along with the weaker band at 1391 cm.$^{-1}$ indicates *t*-butyl groups. The absence of a band at 1380 cm.$^{-1}$ shows the absence of single methyls that would be present in *n*-butyl or *sec*-butyl groups.

As is evident from the regular shift of bands in Fig. 1, the three bands at 2562, 2620 and 2684 Å. agree with the assigned structure, 1,3,5-tri-*t*-butylbenzene.

Physical Property Correlations.—A few simple correlations of some of the other physical properties were made. The 1,3,5-trialkylbenzenes have no vicinal groups to introduce steric factors and hence

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[13] R. B. Barnes, R. C. Gore, R. W. Stafford and V. Z. Williams, *Anal. Chem.*, **20**, 402 (1948).

it can be hoped that the properties will vary smoothly with structure.

A relationship between the boiling point and the molecular weight is shown in Fig. 4. The boiling points, after 10° is added for each first alkyl branch and 5° for each second branch, define a fairly smooth curve. This curve is essentially a graphical representation, and confirmation, of a correlation proposed by Francis.[14]

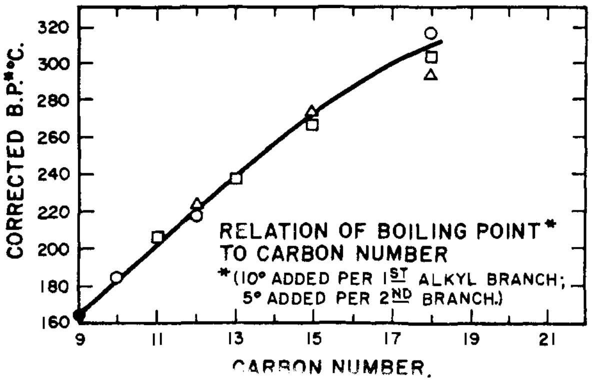

Fig. 4.—Relation of boiling point to carbon number of 1,3,5-trialkylbenzenes.

In Fig. 5, the specific refraction, calculated from the refractive index and density by the equation shown, is plotted against the number of carbon atoms in the molecule. 1,3,5-Trimethylbenzene is considered as the parent compound. The points along the upper curve belong to compounds formed by the replacement of one or more of the methyl groups of 1,3,5-trimethylbenzene by a primary or secondary alkyl group. The points along the lower curve represent compounds formed by the replacement of one or more methyl groups by a *t*-butyl group. The two curves show that normal and secondary groups give a higher specific refraction to the molecule than do tertiary groups.

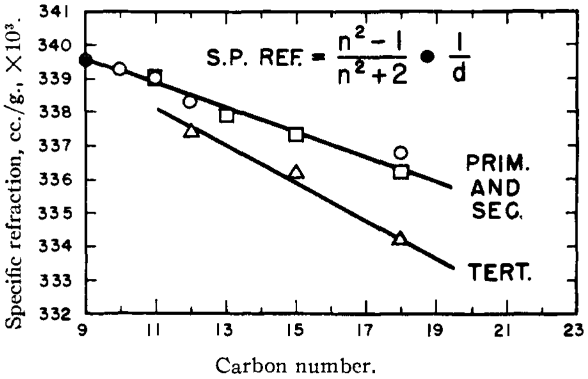

Fig. 5.—Relation of specific refraction to carbon number.

From a theoretical view, these curves are of interest because they show that normal and secondary alkyl groups increase the polarizability of a benzene ring more than do tertiary groups. From a practical view, they could be useful in assigning configuration to unknown trialkylbenzenes.

Acknowledgment.—The authors are indebted to Seymour Meyerson for obtaining and interpreting the mass spectrum; L. J. Schmauch for constructing the automatic slit mechanisms for the infrared spectrometers; Betty Ellen Ries for obtaining the ultraviolet spectra; M. C. Hoff and F. S. Jones for determining melting points; and R. J. Hengstebeck for making valuable suggestions.

WHITING, INDIANA

[14] A. W. Francis, *Chem. Revs.*, **42**, 107 (1948).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Synthesis and Fungistatic Activity of Some 3-Hydroxybiphenyl Derivatives

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The reported toxicity of 2- and 3-phenanthrol toward *Aspergillus niger* has been confirmed and shown to be general for some fluorenols and hydroxybiphenyls. Introduction of an alkyl group into the 4-, 6- or 4′-position of 3-hydroxybiphenyl failed to enhance its fungistatic activity.

Of a group of more than eighty phenanthrene derivatives tested for fungistatic activity against *Aspergillus niger*, Steinberg[1] found 3-phenanthrol to be the most active. Using the same organism but another testing method[2] we have confirmed the high fungitoxic activity of 3-phenanthrol and its superiority in this respect to 2-phenanthrol. Tests on some related fluorenols and hydroxybiphenyls (Table I) revealed that 3-hydroxybiphenyl[3] was equal or superior to any in the group.

It is a well-known phenomenon that the introduction of an alkyl side-chain will often increase the *bactericidal* activity of simple phenols.[4] Thus it seemed worthwhile to determine whether a similar modification in the structure of 3-hydroxybiphenyl might increase its activity toward *A. niger*.

A survey of the literature revealed a description of two alkyl-3-hydroxybiphenyls,[5] formulated as the 4-propyl and 6-propyl derivatives. It has now been shown that the structure postulated for the first is correct while that for the second is erroneous.[6]

[1] R. A. Steinberg, *J. Agr. Research*, **60**, 765 (1940).

[2] J. M. Leonard and V. L. Blackford, *J. Bact.*, **57**, 339 (1949).

[3] The activity of 3-hydroxybiphenyl and its congeners against certain wood-damaging fungi was discussed by I. Hatfield, *Proc. Am. Wood-Preservers' Assoc.*, **31**, 57 (1935).

[4] For a review dealing in part with this subject see C. M. Suter, *Chem. Revs.*, **28**, 269 (1941).

[5] S. E. Harris and W. G. Christiansen, *J. Am. Pharm. Assoc.*, **23**, 530 (1934).

[6] A molecular weight determination but no analysis was reported for the "3-hydroxy-6-propylbiphenyl" of Harris and Christiansen. Both the composition and structure of the product are unknown.