[Contribution from the Research Laboratories of Universal Oil Products Company]

Steric Inhibition of Resonance in 1-Methyl-2-isopropenylbenzene

By M. J. Murray and W. S. Gallaway

The ultraviolet absorption spectrum of benzene in solution shows a number of sharp bands between 240 and 270 mμ. In the spectrum of toluene the absorption is shifted slightly to the red and in di- and polyalkylbenzenes a further shift in that direction is noted. The molecular extinction coefficient at the maximum near 260 mμ for these compounds is of the order of 100–500. A pronounced broad minimum between 230 and 240 mμ is common to the spectra of benzene and alkylated benzene as is also a very intense band near 200 mμ.[1] A lone double bond in an alkyl group on the benzene nucleus, so long as it is not in the α,β-position, has only a minor effect on the spectrum of the aromatic nucleus either as to position or as to intensity. On the other hand, when the olefinic bond of the side chain is conjugated with the ring, as in styrene, very marked changes occur. There is considerable "washing out" of the fine structure so characteristic of the simple aromatic ring and such a large shift toward the red that the 200 mμ band of the benzene nucleus occurs near 250 mμ. The molecular extinction coefficient at the maximum is greater than 10,000. Several weaker bands occur near 290 mμ. The spectra of α- and β-methylstyrenes are similar to that of styrene except that the α-compound is nearly lacking in bands near 290 mμ.

The authors have found that the ultraviolet absorption spectrum of 1-methyl-4-isopropenylbenzene is, in general, also quite similar to that of styrene. The molecular extinction coefficient at 247 mμ, the wave length of the band maximum, is 13,600. There are two definite inflections near 290 mμ. The spectrum of the isomeric ortho hydrocarbon, however, is quite different. There is no absorption maximum between 220 and 290 mμ. A comparison of the two spectra is given in Fig. 1.

A reasonable explanation of this phenomenal difference in spectra can be given on the basis of resonance. In the para compound, the benzene ring and the isopropenyl group are permitted to assume the same plane and thus to resonate. In the ortho compound, the steric relations are such that the two groups cannot lie in the same plane, hence their resonance is inhibited.

Recently the ultraviolet absorption spectra of ortho and para $CH_3C_6H_4CH{=}CHCHOHCH_3$ have been reported.[2] The spectra of these two isomers are very similar and resemble closely that of styrene. It is apparent that here the ortho compound is not sterically prevented from resonating.

It has been pointed out[3] that steric interference with resonance in the case of certain aryl nitro and carbonyl derivatives resulted in Raman spectral shifts to higher frequencies for the stretching vibration of the respective doubly bound groups. In the present work a similar shift was noted in the infrared absorption spectra of the ortho as compared to the para methylisopropenylbenzene. The band which is due to the olefinic stretching vibration near 1600 cm.$^{-1}$ in the para compound where resonance is unhindered is found at 1625 cm.$^{-1}$. The ortho derivative has the band at 1635 cm.$^{-1}$ which is shifted toward that of an unconjugated olefin though the frequency is still considerably lower than that of a completely unconjugated double bond of the same class.

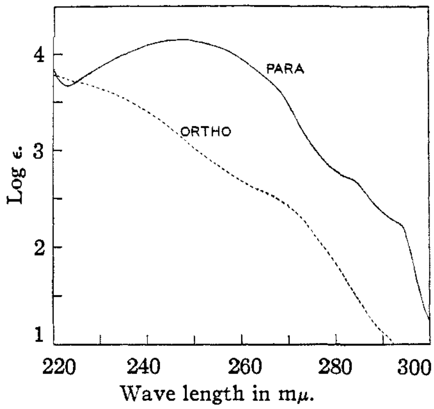

Fig. 1.—Ultraviolet absorption spectra of methylisopropenylbenzenes: ——, para; ------, ortho.

Further confirmation of the steric hindrance by the ortho methyl group on the isopropenyl group is given by the displacement of the deformation frequency of the double bond. Normally, this frequency is found in the neighborhood of 875–890 cm.$^{-1}$ for unsymmetrically disubstituted ethylenes. This is found to be the case for 1-methyl-4-isopropenylbenzene for which the value is 889 cm.$^{-1}$. However, for the ortho compound, the absorption is located at 898 cm.$^{-1}$ which is nearly high enough to be in the region of monosubstituted ethylenes. To prove that the compound was not a monosubstituted ethylene and to establish the authenticity of the sample, the ortho hydrocarbon was hydrogenated and its infrared spectrum obtained. The product was found to be *o*-cymene with no measurable amounts of other hydrocarbons present. The infrared absorption spectra of the ortho and para methylisopropenylbenzenes are given in Fig. 2.

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(1) A review of the ultraviolet absorption studies of aromatic compounds by R. Norman Jones is to be found in *Chem. Revs.*, **32**, 1 (1943).

(2) Braude, Jones and Stern, *J. Chem. Soc.*, 1087 (1947).

(3) Saunders, Murray and Cleveland, This Journal, **63**, 3121 (1941).

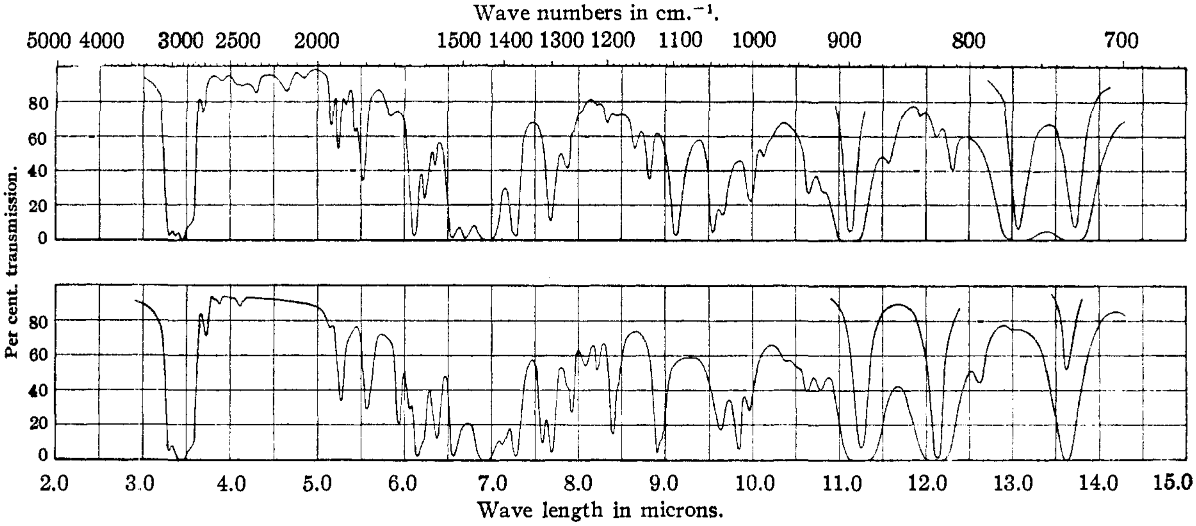

Fig. 2.—Infrared spectra of 1-methyl-2-isopropenylbenzene (upper curve) and 1-methyl-4-isopropenylbenzene (lower curve). Cell lengths, 0.1 mm. and 0.01 mm. in each case.

Experimental

Ultraviolet absorption measurements were made with a Beckman Spectrophotometer, model DU with ultraviolet accessories. Iso-octane, purified by passage through a column of silica gel, was used as solvent. The infrared spectra were obtained on a recording spectrophotometer made by the Gaertner Scientific Corp., very similar, optically, to the instrument described by McAlister.[4]

The 1-methyl-4-isopropenylbenzene boiled at 83° at 18.5 mm.

The 1-methyl-2-isopropenylbenzene boiled at 172–173° at 760 mm. This olefin was reduced by hydrogen at 40 atmospheres at 25° in a rotating autoclave in the presence of UOP nickel on kieselguhr.

Acknowledgment.—Samples of the hydrocarbons were furnished by Dr. Herman Pines of this Laboratory. His cooperation is hereby gratefully acknowledged.

Summary

The ultraviolet absorption spectrum of *p*-methylisopropenylbenzene resembles that of styrene while the spectrum of the ortho isomer does not have the expected maximum near 250 mμ. This difference can be accounted for on the basis that in the ortho compound there is steric interference with the resonance between the benzene ring and the olefinic group in the side chain. A similar conclusion is reached by comparison of the infrared spectra of the two compounds.

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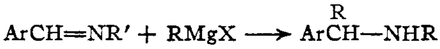
[4] McAlister, Matheson and Sweeney, *Rev. Sci. Instruments*, **12**, 314 (1941).

[Contribution from the Department of Chemistry, University of Notre Dame]

The Reaction of Grignard Reagents with Schiff Bases[1]

By Kenneth N. Campbell, C. H. Helbing,[2] M. Patricia Florkowski[3] and Barbara K. Campbell[4]

Some years ago we became interested in preparing amines of the type ArCH(R)-NHR′. Compounds of this type are not readily available by the conventional methods for making secondary amines. The Leuckart reaction with substituted formamides can be used, but the yields are low.[5] The reaction of 1-aryl-1-halo-alkanes with primary amines can also be used, but here also the yields are frequently low, as halides of this type tend to form olefins in the presence of basic reagents. The most feasible synthesis of amines of this type seemed to be the reaction of a Grignard reagent with the Schiff base formed from an aromatic aldehyde and an aliphatic primary amine


$$\mathrm{ArCH{=}NR' + RMgX \longrightarrow Ar\overset{R}{C}H{-}NHR'}$$

At the time this work was started, very little information had been published on this reaction. Busch and Leefheim[6] had synthesized a few amines in this way, and Grammaticakis[7] had also used the reaction to some extent.

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[1] This paper was presented before the Medicinal Division at the Chicago A. C. S. meeting, April, 1948.

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[5] Goodson, Weigand and Splitter, This Journal, **68**, 2174 (1946).

[6] Busch and Leefheim, *J. prakt. Chem.*, **77**, 20 (1908).

[7] Grammaticakis, *Compt. rend.*, **207**, 1224 (1938).