

Steric Effects in the Ultraviolet Absorption Spectrum of Mesityl Methyl Ether

BY EDWARD A. FEHNEL¹ AND MARVIN CARMACK

In connection with our studies of the ultraviolet absorption spectra of various phenyl sulfides, which are reported elsewhere,^{2,3} we have had occasion to examine the spectra of several analogous phenyl ethers. Since no previous example of the spectrum of an *o*-alkyl-substituted phenyl ether seems to have been recorded in the literature, we are reporting our results with mesityl methyl ether.

The absorption spectra of mesityl methyl ether, *p*-tolyl methyl ether and mesitylene are compared in Figs. 1 and 2. The introduction of a *p*-methyl substituent into anisole⁴ results in the expected bathochromic shift ($\Delta\lambda$ ca. 6–8 $m\mu$) without any significant change in the intensity at the absorption maxima. Further substitution of two methyl groups in the ortho positions, as in mesityl methyl ether, however, results in the suppression of the absorption in the region 260–285 $m\mu$ and a

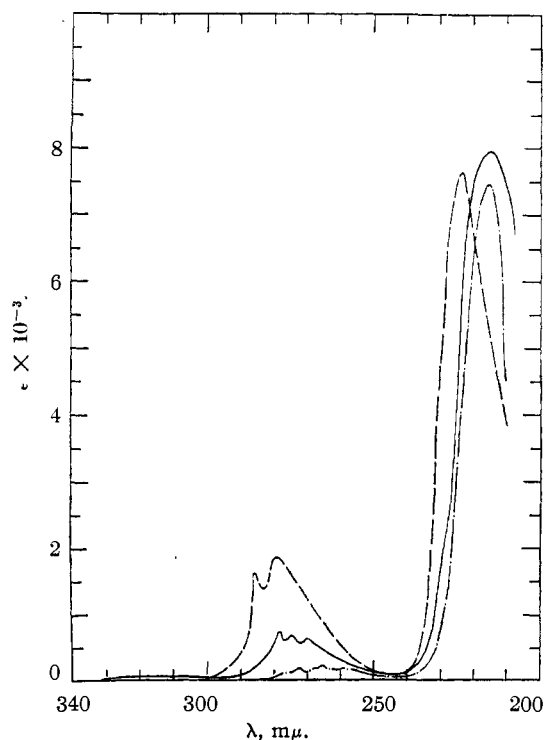


Fig. 1.—Absorption spectra: mesityl methyl ether, —; *p*-tolyl methyl ether, - - - -; mesitylene, - · - · -; all in ethanol.

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(2) Fehnel and Carmack, *THIS JOURNAL*, **71**, 84 (1949).

(3) Fehnel and Carmack, *ibid.*, **71**, 2889 (1949).

(4) Absorption data for anisole has been reported by several investigators; see, for example, Scheibe, Backenköhler and Rosenberg, *Ber.*, **29B**, 2617 (1926); Wolf and Herold, *Z. physik. Chem.*, **B13**, 201 (1931); Doub and Vandenbelt, *THIS JOURNAL*, **69**, 2714 (1947).

general displacement of the curve toward shorter wave lengths. It is particularly interesting to note that the intense absorption band at short wave lengths (*i. e.*, the "primary band," which Doub and Vandenbelt⁵ have shown to be particularly suitable as a basis for comparison of spectra) reaches a maximum at exactly the same wave length (215 $m\mu$) as in the spectrum of the parent hydrocarbon, mesitylene. This behavior appears to be characteristic of compounds in which steric effects interfere with the attainment of the coplanar configuration of the molecule required by resonance theory.⁶

When the spectrum of mesityl methyl ether is plotted on a logarithmic ($\log \epsilon$) basis, as in Fig. 2, a low intensity band with a maximum at 315 $m\mu$ becomes evident. This long wave length band, which is not observed in the spectra of the unsubstituted phenyl alkyl ethers or in that of *p*-tolyl methyl ether, does not seem to arise from the presence of an impurity in the spectral sample, since redistillation failed to produce any change in the spectrum. This anomalous behavior suggests further study of the spectra of other phenyl ethers in which steric inhibition of resonance might be anticipated.

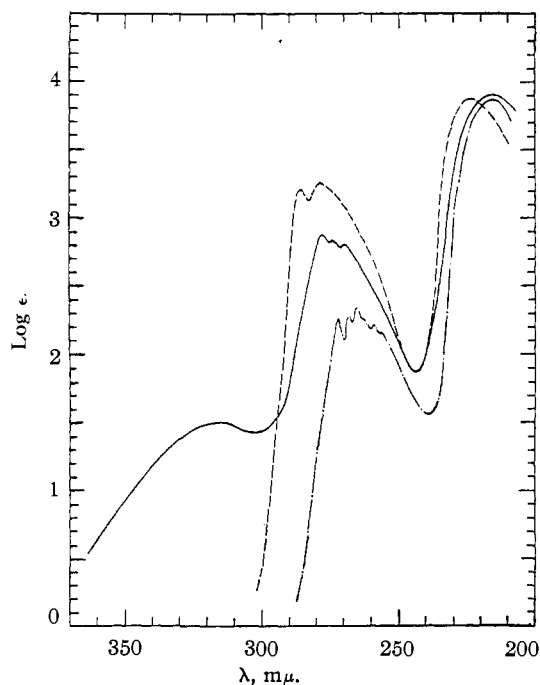


Fig. 2.—Absorption spectra: mesityl methyl ether, —; *p*-tolyl methyl ether, - - - -; mesitylene, - · - · -; all in ethanol.

Experimental

The ultraviolet absorption measurements were made as described in a previous paper,² using

(5) Ref. in footnote 4.

(6) Cf. Remington, *THIS JOURNAL*, **67**, 1838 (1945); Brown and Reagan, *ibid.*, **69**, 1032 (1947).

absolute ethanol as the solvent. The compounds examined were purified by fractional distillation immediately before determination of the spectra. In the case of mesityl methyl ether, the original sample was redistilled and the spectrum redetermined; identical results were obtained with both samples. The wave lengths and logarithms of the molar extinction coefficients at the absorption maxima and at prominent points of inflection are listed in Table I.

TABLE I
ULTRAVIOLET ABSORPTION DATA

Compound	Source ^a	λ , (m μ) ^{Maxima^b}	Log ϵ
Mesityl methyl ether	1	315	1.50
		278	2.88
		274	2.83
		270	2.80
		215	3.90
<i>p</i> -Tolyl methyl ether	2	286	3.21
		279	3.27
		223	3.88
Mesitylene ^c	2	272	2.26
		268	2.26
		265	2.34
		(262)	2.24
		259	2.21
		(256)	2.17
		215	3.87

^a Source references: (1) Biedermann and Ledoux, *Ber.*, 8, 57 (1875); (2) Eastman Kodak Co., redistilled.

^b The wave lengths in parentheses refer to inflection points.

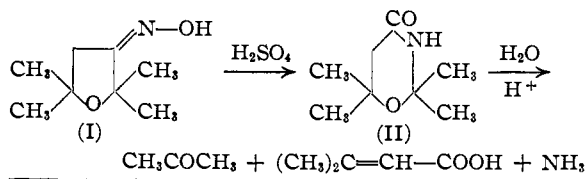
^c Cf. Conrad-Billroth, *Z. physik. Chem.*, B29, 170 (1935); Pickett, Walter and France, *THIS JOURNAL*, 58, 2296 (1936).

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Beckmann Rearrangement of 2,2,5,5-Tetramethyltetrahydro-3-furanone Oxime

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Previous work made available a liberal sample of 2,2,5,5-tetramethyltetrahydro-3-furanone.¹ It was thought that the Beckmann rearrangement of its oxime² (I) would prove of interest because the anticipated lactam (II) should undergo ring cleavage in the process, leading ultimately to acetone, ammonia and β,β -dimethylacrylic acid. These are indeed the products of the reaction with moderately strong sulfuric acid.



(1) Froning and Hennion, *THIS JOURNAL*, 62, 653 (1940).

(2) Dupont, *Ann. chim.*, [8] 30, 536 (1913).

This confirms the instability of (II) and indicates that the oxime (I) has the *trans* structure, perhaps on account of the steric effect of the neighboring *gem*-dimethyl group.

Experimental

A solution of 5 g. of the oxime (m. p. 122–123°)³ in 10 ml. of approximately 77% sulfuric acid in a Claisen flask was heated while nitrogen was bubbled through it. Vigorous reaction occurred and about 3 ml. of distillate was recovered in the receiver cooled in a salt-ice mixture. After drying with calcium chloride (0.95 g. recovered), the boiling point (micro) was 62° and the n_D^{20} 1.381. Qualitative tests indicated that it was chiefly acetone. In a duplicate run the distillate was treated with 2,4-dinitrophenylhydrazine; the derivative was obtained in 64% yield based on the oxime used and melted at 123–124°.

Ammonia liberated from one of the above sulfuric acid solutions, collected and titrated in the usual way, showed a 55% yield.

The alkaline residue from the ammonia distillation was filtered from a small amount of tar and extracted with ether (discarded). The aqueous solution was then acidified with sulfuric acid and extracted twice with 20-ml. portions of ether. The ether extract was dried with calcium chloride and the ether evaporated, leaving 0.75 g. of residue which soon crystallized. This material was purified by solution with potassium carbonate, reprecipitation with hydrochloric acid and crystallization from petroleum ether. Small needles melting at 66–67° were thus obtained. The bromine addition product melted at 105–106°. Ustinoff⁴ gives 69.5–70° and 105–106° as the melting points of β,β -dimethylacrylic acid and its dibromide, respectively.

(3) Dupont³ gives 128°.

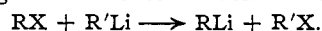
(4) Ustinoff, *J. prakt. Chem.*, [2] 34, 478 (1886).

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Halogen-Metal Interconversions with Halogenated Anilines and Anilides

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In connection with studies concerned with the introduction of variously substituted aryl groups into organolead compounds, it was desirable to prepare organolithium compounds containing functional groups such as amino or alkylamino. A method of choice for the synthesis of such types is the halogen-metal interconversion reaction.²



The halogen compounds studied in the present investigation are *o*-bromoaniline, *p*-bromoaniline, *p*-bromo-*N*-methylaniline and *N*-(*p*-iodophenyl)-phthalimide. In each instance a diethyl ether solution of *n*-butyllithium was added to the halogen compound dissolved in diethyl ether. The reaction mixture was carbonated and the resulting acid isolated as such or as the benzenesulfonamide. Details are given in the experimental section.

The previously reported reaction of *n*-butyl-

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(2) (a) Gilman and Stuckwisch, *THIS JOURNAL*, 64, 1007 (1942); (b) Gilman and Arntzen, *ibid.*, 69, 1537 (1947); (c) Gilman and Melstrom, *ibid.*, 70, 4177 (1948); (d) for general references, see pp. 538–539 of Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943.