

be handled safely. Operations involving VII should be conducted behind a safety shield.

A solution of 5.9 g of sodium azide in 45 ml of water was stirred at ca. 15° during the dropwise addition of 7.9 g of crude 2-methyl-5-nitroisophthaloyl chloride in 30 ml of acetone. Water (15 ml) was added, and the mixture containing precipitated VII was stirred at ambient temperature for 30 min. The cream-colored solid (VII) was removed by filtration and washed with cold water (**Caution!** VII is left damp with water, see note above). VII decomposed violently at 75° when an attempt to determine the melting point was made. Thin-layer chromatography (silica gel HF-254 with benzene as eluant) indicated VII was pure since only one spot was present.

The *damp* acyl azide (VII) was added in small portions to 150 ml of absolute ethanol stirred at 60°. Nitrogen gas was evolved, and the ethanol solution was then heated to boiling for 10 min. The hot solution was filtered, and the filtrate cooled in ice to give 5.6 g (60.0%) of ethyl 4-nitrotoluene-2,6-dicarbamate (VIII), mp 204–205°. NMR and mass spectral data confirmed that VIII is the dicarbamate (Table I).

A mixture of 5.5 g of VIII, 5.5 g of potassium hydroxide, 55 ml of water, and 55 ml of ethanol was heated at reflux for 3 h. The cooled reaction mixture was filtered, and the red crystals of 2,6-diamino-4-nitrotoluene (I) were washed with water. The red crystals (mp 213–215°) weighed 2.55 g (86.4%). Crystallization from acetone–water raised the melting point to 214–216°.

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NMR Spectra of Some Methyl-Substituted Diaryliodonium Compounds

Reuben L. Baumgarten* and Norman F. Bray*

The John Paul Clay Laboratories of the Department of Chemistry, Herbert H. Lehman College, City University of New York, Bronx, N.Y. 10468

The NMR spectra of a number of methyl-substituted diaryliodonium compounds are recorded and discussed. The effects of the positively charged iodine atom on the spectra are compared to similar effects due to the presence of a carbonium ion.

In recent years there has been some interest in the synthesis and properties of diaryliodonium compounds (1–3, 7). In the course of some studies on these compounds, it was discovered that no NMR spectra have been reported. We now report the spectra of some symmetrical and unsymmetrical diphenyliodonium compounds bearing methyl substituents.

Experimental

The compounds were all synthesized by the methods devised by Beringer (4, 5). The NMR spectra were recorded on a Perkin-Elmer R-12 spectrometer, using saturated solutions of the compounds in deuteriochloroform containing 1% (v/v) of TMS. All peak positions were measured in ppm relative to TMS ($\delta_{\text{TMS}} = 0$). The NMR spectra of these compounds are relatively simple, but reveal certain interesting features.

As shown in Table I, the positively charged iodine atom produces the expected low field shift of the methyl and aromatic protons found in the work on carbonium ion species (8, 10–13). This can be seen by comparing the peak positions in the spectra of the 4,4'-dimethyldiphenyliodonium compounds and the spectrum of iodotoluene. This shift is 0.2–0.4 ppm to

low field for the aromatic protons and 0.05–0.1 ppm to low field for the methyl protons, and is analogous to a shift of ca. 2.5 ppm to low field for the carbonium ion species relative to benzene (9, 10). (A better analogy might be with ammonium or sulfonium salts which, like iodonium ions, are closed shell cations.) While a direct comparison is not possible because the spectra of the carbonium ions are run in different solvents and, frequently, at different temperatures due to their general instability, the magnitude of these shifts is to be expected based on the relative size difference of the carbon and iodine species involved.

Because of the decreased solubility of the higher substituted diphenyliodonium compounds in deuteriochloroform, the bromide salt was frequently used in place of the less soluble iodide. No major differences in the NMR spectra are expected due to a difference in these anions, as shown by a comparison of the data for the bromide and iodide salts of 4,4'-dimethyldiphenyliodonium compounds and the 2,2',4,4',6,6'-hexamethyldiphenyliodonium (Table I).

The methyl region of the spectra for all compounds run shows absorption in only two principal regions: 2.55–2.65 ppm, due to the methyl groups ortho to the positively charged iodine atoms, and 2.25–2.35 ppm, due to the meta and para methyl groups. No distinction could be made between the absorptions due to the meta and para methyl groups.

The aromatic region of the spectra shows the characteristic patterns of substituted benzenes. The aromatic protons of the 4,4'-dimethyldiphenyliodonium compounds give rise to a

Table I. NMR Spectral Data of Methyl-Substituted Diaryliodonium Compounds

Compound ^a	Mp, °C ^b	Anion	NMR data, δ , ppm ^c		
			Methyl protons ^d	Aromatic protons	Other ^e
4,4'- Dimethyldiphenyliodonium	186-7	Br	2.30	7.04, 7.17 7.81, 7.95	2.05, 2.15 2.61, 7.29
	168-9	I	2.32	7.08, 7.21 7.82, 7.97	2.63, 7.29
2,4',5- Trimethyldiphenyliodonium	155-6	I	2.30 (2)	7.01, 7.16	1.70
			2.58	7.19, 7.25 7.71, 7.85, 7.88	
2,4,4',6- Tetramethyldiphenyliodonium	173-4	Br	2.28 (2)	6.98, 7.12, 7.24	...
			2.65 (2)	7.58, 7.72	
2,2',4,4',6,6'- Hexamethyldiphenyliodonium	125-6	Br	2.26 (2)	6.96	2.35, 2.41 6.85, 7.24
			2.56 (4)		
			111-14		
<i>p</i> -Iodotoluene ^f			2.24	6.78, 6.91 ^g 7.44, 7.58	...
Mesitylene ^f			2.21	6.78	...
			2.15 (Neat)	6.68	...

^a The iodonium compounds were run as saturated solutions in CDCl₃ containing 1% (v/v) TMS. ^b See ref. 4. ^c $\delta_{\text{TMS}} = 0$. ^d Value in parentheses indicates the number of methyl groups. ^e These peaks represent minor impurities and in no way alter the interpretation of the spectra. ^f Eastman Organic Chemicals; used without further purification. ^g Expansion shows each line of the low field doublet to be a triplet; the high field doublet shows only a broadening of the lines.

symmetrical doublet of triplets which is characteristic of an A₂X₂-type spectrum. The low field peaks are assigned to the ortho protons based on their proximity to the positively charged iodine atom. The ortho protons undergo a more pronounced low field shift than the meta protons when compared to their corresponding position in the spectrum of *p*-iodotoluene.

A comparison of the 2,2',4,4',6,6'-hexamethyldiphenyliodonium compounds reveals the magnetically equivalent protons in the iodonium compounds to be a singlet positioned approximately 0.2 ppm down field with respect to their position in mesitylene.

The 2,4,4',6-tetramethyldiphenyliodonium compounds give a spectrum in the aromatic region which is a composite of the spectrum of the 4,4'-dimethyldiphenyliodonium and the 2,2',4,4',6,6'-hexamethyldiphenyliodonium compounds with one major difference. The ortho protons in the tolyl substituted ring of the 2,4,4',6-tetramethyldiphenyliodonium compound are approximately 0.2 ppm up field in comparison to the ortho protons in the 4,4'-dimethyldiphenyliodonium compounds, whereas the meta protons are shifted approximately 0.1 ppm downfield. An examination of a Framework Molecular Orbital model (6) of the 2,4,4',6-tetramethyldiphenyliodonium compound suggests that this difference may be attributed in part to the molecular geometry of the methyl groups in the ortho and meta positions.

The 2,4',5-trimethyldiphenyliodonium compound shows a complex aromatic region which is suspected to be a superposition of an A₂X₂ (tolyl ring) and an AB₂ (xylyl ring) type spectra. In this compound this position of the low field peaks is midway between the maximum and minimum values found in the other compounds. The absorption frequencies of the high field portion of the aromatic region in the tolyl ring ap-

pear to be similar with respect to the frequencies found in the 4,4'-dimethyldiphenyliodonium compounds.

In summary, the spectra of these compounds indicate that the effect of the positively charged iodine atom exerts some influence on the absorption frequencies in the NMR spectra of these compounds; however, the magnitude of this effect appears to be less than that observed in the work on various carbonium ion species.

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