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Preparation of Sterically Hindered Nitrosobenzenes

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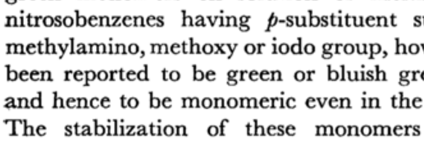
It is well known that most aromatic nitroso compounds exist as colorless or pale yellow dimers in the solid state and dissociate into green or bluish green monomers on solution or melting.[1] Some nitrosobenzenes having *p*-substituent such as dimethylamino, methoxy or iodo group, however, have been reported to be green or bluish green crystals and hence to be monomeric even in the solid state. The stabilization of these monomers has been attributed to the resonance interaction between the nitroso group and the *p*-substituent.[2]

It has been generally concluded that, regardless of the state, the green color (the presence of the n-π^* band) is an evidence of the monomer, and lack of color (the absence of the n-π^* band) indicates the dimer.[1,2]

This paper describes the preparation of a new group of nitrosobenzenes which exist as monomers even in the solid state for steric reasons.

Oxidation of 2,4,6-tri-*t*-butyl-,[3] 2,4-di-*t*-butyl-6-methyl-,[4] 2,5-di-*t*-butyl-,[5] 2,4-di-*t*-butyl-[6] and 4-benzoyloxy-2,6-di-*t*-butylaniline[7] with two molar amount of peroxybenzoic acid in dichloromethane at 0°C gave the corresponding nitroso compounds in good yields.



I: $R_1=R_3=t\text{-Bu}$, $R_2=H$
II: $R_1=t\text{-Bu}$, $R_2=H$, $R_3=CH_3$
III: $R_1=R_3=H$, $R_2=t\text{-Bu}$
IV: $R_1=OCOC_6H_5$, $R_2=H$, $R_3=t\text{-Bu}$
V: $R_1=t\text{-Bu}$, $R_2=R_3=H$

Among them I, II, III and IV were green crystals, and V was green liquid which solidified at dry-ice temperature to give green solid. Their yields, melting points, analytical data and electronic spectra are summarized in Table 1.

From studies on electronic spectra of a number of aromatic nitroso compounds, Nakamoto,[2a] Havinga[2b] and Lüttke[2c] have concluded that electron-donating groups in the *para*-position enhanced the stability of the monomers, and steric hindrance due to the *ortho*-substituents stabilized the dimer.[8] As an example, 2,4,6-trimethyl- and 2,4,6-trichloronitrosobenzenes are colorless dimers in the crystalline state, and the dimer exists in the extent of 70% and 20% in 0.1 M solution at 20°C, respectively.[2c] Accordingly, the extinction coefficients of their n-π^* absorption maxima exhibit appreciable change with varying concentration.[2b]

Contrary to anticipation that *ortho*-substituents would stabilize the dimers, nitrosobenzenes I—V having more bulky *ortho*-*t*-butyl groups seem to be monomeric even in the solid state, because they are highly colored in that state. In order to eliminate the possibility that they are mixtures of the monomer and the dimer, their electronic spectra were measured at various concentrations for I—IV, for the values of their extinction coefficients would increase upon dilution if they contain the dimeric species. As shown in Table 2 their extinction coefficients were almost invariable, no regular change being exhibited.

On the basis of the results described above, it is reasonably concluded that I—V are so sterically hindered by the bulky *t*-butyl groups that they cannot dimerize even in the solid state unlike methyl- or halogeno-substituted nitrosobenzenes.

In the course of our investigation of the oxidation of sterically hindered anilines to the corresponding nitrosobenzenes, we have found that peroxybenzoic

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[8] The same conclusion has also been reached from cryoscopic measurement.[9]

[9] D. L. Hammick, *J. Chem. Soc.*, **1931**, 3105.

TABLE 1. YIELDS, MELTING POINTS, ABSORPTION MAXIMA DUE TO THE n-π^* TRANSITION AND ANALYTICAL DATA OF NITROSOBENZENES

Compd.	Yield (%)	Mp (°C)	$\lambda_{max}^{n\text{-hexane}}$		Analyses (%)*		
			mμ	ε	C	H	N
I	80	167—168	765	56.7	78.25 (78.49)	10.81 (10.61)	4.93 (5.09)
II	53	27—29	810	39.1	77.41 (77.20)	10.24 (9.94)	6.15 (6.00)
III	68	28—30	790	35.0	76.39 (76.66)	9.47 (9.65)	6.39 (6.39)
IV	43	85—87	761	51.7	74.21 (74.31)	7.21 (7.42)	4.30 (4.13)
V	73	liquid	790	54.8	76.38 (76.66)	9.97 (9.65)	6.47 (6.39)

* Values in parentheses are calculated values.

TABLE 2. EXTINCTION COEFFICIENTS IN THE n-π^* BAND OF NITROSOBENZENES AT VARIOUS CONCENTRATIONS

I		II		III		IV	
Concn.*	ε	Concn.*	ε	Concn.*	ε	Concn.*	ε
0.0163	58.9	0.0161	41.3	0.0296	34.6	0.0185	51.9
0.00945	55.3	0.00805	39.0	0.0134	35.4	0.0112	52.5
0.00652	55.7	0.00403	37.7	0.00535	35.5	0.00632	50.2
0.00130	56.9	0.00161	38.5	0.00107	34.6	0.00165	52.0

* in mol/*l*.

acid is the best reagent.[10] Oxidation of 2,4,6-tri-*t*-butylaniline with Caro's acid and peroxyacetic acid,[11] which are common oxidizing agents[1] for changing anilines to nitrosobenzenes, was unsuitable to give the corresponding nitrosobenzene.

Experimental

Melting points are uncorrected. The electronic spectra were recorded on a Hitachi recording spectrophotometer Model EPS-3.

General Preparation of Nitrosobenzenes. To ice-cooled dichloromethane solution of anilines was added dropwise with stirring two molar amount of peroxybenzoic acid in the same solvent. After being kept at 0°C overnight, the reaction mixture was shaken with aqueous sodium carbonate to remove benzoic acid. The organic layer was dried over anhydrous sodium sulfate, and then the solvent was evaporated. The crude product thus obtained was purified by means of column chromatography on silica gel; nitrosobenzenes were eluted with petroleum ether. In the case of 2,4,6-tri-*t*-butylnitrosobenzene (I) alumina was preferable because of good separation of nitrosobenzene from nitrobenzene as a by-product. (I) was recrystallized from methanol. Yields, melting points, electronic spectra and analytical data of purified nitrosobenzenes are summarized in Table 1.

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10) As for peroxybenzoic acid there have been a few investigations[12] dealing with the reaction only qualitatively except for the studies by Horner,[12c] who reported azobenzene and azoxybenzene as the reaction products with aniline.

11) R. R. Holmes and R. P. Bayer, *J. Am. Chem. Soc.*, **82**, 3454 (1960).

12) a) A. Baeyer and V. Villiger, *Ber.*, **33**, 1569 (1900). b) N. Prileschajew, *ibid.*, **42**, 4811 (1909). c) L. Horner and W. Kirmse, *Ann.*, **597**, 70 (1955).