Hexamethylazoxybenzene. Structure, Basicity, and Rearrangement[1]

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2,2′,4,4′,6,6′-Hexamethylazoxybenzene (**1**) has been prepared and characterized. The u.v. spectrum is indicative of large distortion from coplanarity. **1** is only slightly more basic than azoxybenzene despite expectations due to electronic effect of the methyl substituents. Two factors are considered responsible for this: steric inhibition of resonance in the unprotonated species and steric hindrance to hydration in the conjugate acid.

Rearrangement of **1** in moderately concentrated sulfuric acid gives rise to the alcohol 4-hydroxymethyl-2,2′,4′,6,6′-pentamethylazobenzene (**6**). A Bamberger type phenolic product which would result from methyl migration is not observed. Possible reaction mechanisms are given.

L'hexaméthyl-2,2′,4,4′,6,6′-azoxybenzène (**1**) a été préparé et caractérisé. Le spectre u.v. indique une forte distorsion par rapport au plan. **1** n'est que légèrement plus basique que l'azoxybenzène malgré l'effet électronique attendu des substituants méthyles. Deux facteurs ont été considérés comme responsables de cet état: l'inhibition stérique à la résonance dans l'espèce non protonée et l'empêchement stérique à l'hydratation dans l'acide conjugué.

Le réarrangement de **1** dans l'acide sulfurique de concentration moyenne conduit à l'alcool hydroxyméthyl-4 pentaméthyl-2,2′,4′,6,6′ azobenzène (**6**). Un produit phénolique de type Bamberger résultant de la migration de méthyle n'a pas été observé. Des mécanismes possibles pour la réaction ont été donnés.

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As part of a continuing study on structure and reactivity of azoxy compounds (1, 2), we have prepared for the first time the symmetrically polysubstituted derivative 2,2′,4,4′,6,6′-hexamethylazoxybenzene, **1**. We report in this paper on the spectral characteristics of **1**, on its basicity as defined by eq. 1, and on its rearrangement.

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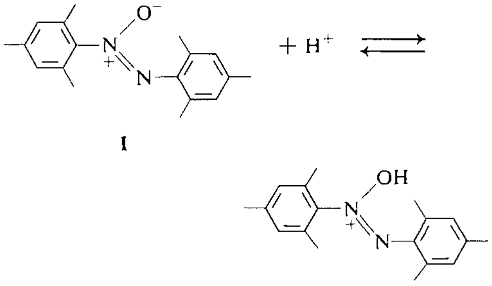

1

2

Spectral Characterization

The compound **1**, prepared by oxidation of the hexamethylazobenzene, has the u.v.-visible spectral characteristics given in Table 1. The assignments of the bands are similar to previous designations (3–5). The E_1 band is an electronic transition of the benzene rings, the E_2 band probably involves the azoxy function and one of the benzene rings, while the K band represents a $\pi \rightarrow \pi^*$ transition involving the entire conjugated system. For purposes of comparison Table 1 also contains the K-band data for azoxybenzene, and for some dialkyl derivatives.

It is seen that the K band in **1** is shifted to shorter wavelength, relative to azoxybenzene, and the extinction coefficient is considerably smaller. This effect is also observed with the 2,2′-dialkyl azoxybenzenes, though to a lesser extent, but it is reversed with the 4,4′-dialkyl azoxybenzenes. The bathochromic shift in the K band for the 4,4′-azoxybenzenes has been attributed in the past to operation of the inductive effect (6) and the hyperconjugative effect (3). On the other hand, the hypsochromic shift and the diminution in absorption intensity of the K band which is observed with the 2,2′-dialkyl azoxybenzenes has been generally attributed to steric hindrance to coplanarity, since steric inhibition of resonance would raise the energy level of the excited state relative to the ground state, and to reduced overlap between the π and π^* orbitals.

The distortion from coplanarity (deformation

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[1] Part XI in a series on the Wallach rearrangement. For Part X see ref. 1.

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TABLE 1. Spectral characteristics of substituted azoxybenzenes

Azoxybenzenes[a]	λ (nm)	ε	Band	Δλ	Δε	θ(°)
2,2′,4,4′,6,6′-Hexamethyl	214(s)	18 300	E_1			
	240(s)	7 500	E_2			
	307	3 800	K	−16	−10 700	67
4,4′-Dimethyl	330	18 100	K	+7	+3 600	—
2,2′-Dimethyl	312	11 100	K	−11	−3 400	38
4,4′-Diethyl	334	20 700	K	+11	+6 200	—
2,2′-Diethyl	309	9 300	K	−14	−5 200	48
Unsubstituted	323	14 500	K	0	0	—

[a]Data for 2,2′,4,4′,6,6′-hexamethylazoxybenzene are from the present work and refer to methanol solvent. The rest of the data are taken from the literature (3, 6).

angle, θ) may be calculated from the diminution in the molar extinction of the K band, according to the relationship[3] (7), $\cos^2\theta = \varepsilon/\varepsilon_0$. In this equation ε is the molar extinction coefficient for the ortho-substituted derivative while ε_0 is the value for the para-substituted analog; this assumes that the electronic effect of the substituent(s) is independent of the position of substitution (ortho or para) and that in the absence of steric effects the extinction coefficients for the two isomers should be the same. Application of this relationship to the dimethyl- and diethylazoxybenzenes leads to deformation angles of 38 and 48°, respectively (3, 6).

The choice of a reference model in the present study provides a difficulty. If one assumes, as has been done previously (6), that the contribution of each alkyl group is additive, then the theoretical decrease in intensity would be given by $+3600 \times 3 = +10\,800$, so that in the absence of steric effects the extinction coefficient for **1** should be $14\,500 + 10\,800 = 25\,300$. Hence θ is calculated from the relationship $\cos^2\theta = 3800/25\,300$ which yields $\theta = 67°$. Though the absolute value is somewhat in doubt, it is clear that **1** has the largest distortion so far observed in the azoxybenzene series. It may be noted that X-ray structure data give an angle of twist of 22.6° for 4,4′-dimethoxyazoxybenzene (9) so that the calculated deformation angles shown in Table 1 should all be augmented correspondingly.

Basicity

The pK_a of **1** was determined by the spectrophotometric method employed previously (10).

TABLE 2. Spectral data for pK_a measurements

H_2SO_4[a] (*M*)	H_0[b]	A_{BH^+}[c]	A_B[d]	I[e]
6.57	−3.14	0.110	0.275	—
7.34	−3.63	0.210	0.542	0.092
8.25	−4.20	0.187	0.412	0.058
8.92	−4.60	0.288	0.458	0.228
9.24	−4.77	0.381	0.492	0.441
9.52	−4.93	0.470	0.465	0.728
10.20	−5.27	0.682	0.412	2.29
10.73	−5.51	0.789	0.345	5.07
11.35	−5.80	0.868	0.310	15.1
11.61	−5.90	0.885	0.305	23.8
12.32	−6.21	0.903	0.290	58.3

[a]Contains 5% dioxane.
[b]Data from ref. 11.
[c]Absorbance at 378 nm.
[d]Absorbance at 306 nm.
[e]Ionization ratio, $I = (A - A_B/A_{BH^+} - A)$, calculated at 378 nm, using $A_B = 0.145$ and $A_{BH^+} = 0.916$ (see text).

The acidic medium used was aqueous sulfuric acid containing 5% dioxane, the organic co-solvent being required in order to enhance solubility of the substrate. An H_0 scale applicable to this medium is available (11).

Protonation of **1** is characterized by appearance of an absorption maximum in the 387 nm region due to species **2**. Measurements over a range of acid concentrations give a typical sigmoid curve when A_{387} is plotted against H_0 (data of Table 2). One thus obtains a pK_a of −5.02 corresponding to the H_0 value at the inflection point.[4] Absorbances at 307 nm corresponding to the unprotonated species did not show a consistent decrease with increased acidity, possibly due to a selective medium effect since isosbestic point behavior was not observed. The Davis–Geissman (12) procedure was therefore not deemed applicable. However,

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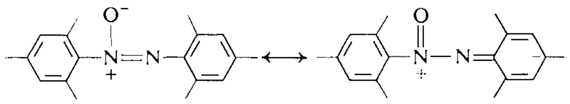
[3] The alternative relationship $\cos\theta = \varepsilon/\varepsilon_0$ has also been proposed (8) and leads to somewhat larger values of the deformation angle θ. For consistency with previous work (3, 6) we use the relationship given in the body of the text.

[4] The measured pK_a refers to the H_0 value at 50% protonation rather than to the thermodynamic dissociation constant.

the smooth sigmoid curve of A_{387} *vs.* H_0 yielded values of ε_B and ε_{BH^+} which were then used to calculate ionization ratios over the acidity region examined. The log I *vs.* H_0 plot is linear with a slope of 1.51. A pK_a value of -5.02 is obtained from this plot corresponding to log $I = 0$, in good agreement with the value derived from the A_{387} *vs.* H_0 plot. The "Hammett slope" of 1.51 is considerably higher than the value 1.0 recorded for azoxybenzene and 0.9–1.0 for the naphthyl azoxy series (10), though it is well within the range of slope values compiled by Bunnett and Olsen for a variety of organic bases (13). Apparently **1** is a poor Hammett base, which could be due to the abnormal amount of twist in this molecule. The different acidity response of **1** compared to azoxybenzene, as reflected in the dependence of log I on H_0, is thus not too surprising.

It is of interest to discuss the basicity of **1** in terms of structural and electronic effects and to compare the pK_a value with that of the parent azoxybenzene. For that purpose the measured pK_a of **1** may be reduced to the value applicable to aqueous medium by means of an appropriate correction factor (11), which then yields pK_a (aq) = -4.85. It follows that **1** is a stronger base than azoxybenzene, pK_a (aq) = -5.15, but only moderately so. Qualitatively, one can account for the increased basicity of **1** by examining the possibility of delocalization of charge due to contribution by canonical structures such as the following:



1*a* 1*b*

The electron-releasing effect of methyl will result in diminished importance of structures such as **1***b*. The consequent increased charge density on the azoxy oxygen relative to that of azoxybenzene should lead to **1** being more basic than azoxybenzene, which is as observed. A more complete treatment should also consider inductive and steric effects.

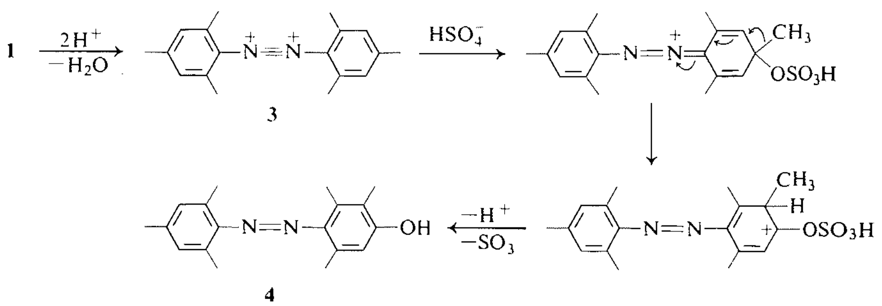
However, quantitatively, the increased basicity of **1** over that of azoxybenzene is far less than might have been anticipated. The data of Hahn and Jaffé (14) on the pK_a of substituted azoxybenzenes show that 4,4′-dimethylazoxybenzene has increased basicity by almost 1 pK unit over that of azoxybenzene. If one assumes the effect of the methyl substituents to be additive then the calculated pK_a of **1** would be around -2.

It is probable that the variance between the anticipated and the actual pK_a value of **1** is due, in part, to steric inhibition of resonance. Thus to the extent that the methyl groups cause distortion from planarity in the molecule, the hyperconjugative capability of these methyls will become diminished. The second factor to be considered is steric hindrance to hydration (15). Since the protonated form of the base will be more hydrated by solvent molecules than the neutral form, the presence of the ortho methyl groups in **1** will interfere with solvation of the protonated azoxy function and hence destabilize the protonated form. This factor will also result in decreased basicity relative to the situation in azoxybenzene. Corroboration of the role of this factor in the present system is indicated by a negative ϕ value (-0.55) when the data are plotted according to the procedure of Bunnett and Olsen (13), which is indicative of less than optimum hydration of the BH^+ species. The hydration factor may well weigh the most heavily in reducing the basicity of **1** (cf. ref. 16).

Acid Catalyzed Rearrangement

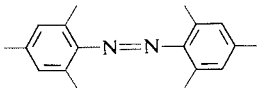
Investigation of the Wallach rearrangement of **1** in acidic media promised to be of particular interest since a "normal" type rearrangement (2), whereby hydroxyl enters a vacant ortho or para position, is precluded in this system. It appeared possible, however, that an alternative pathway would prevail, with a methyl group migrating from a para to a meta position, as indicated in Scheme 1. This pathway is based on a presumed analogy with the Bamberger rearrangement of substituted phenyl hydroxylamines in acid media where methyl migration follows nucleophilic attack thus leading to a rearranged phenolic product (17, 18). The proposal of initial formation of the dication **3** is by analogy with our previous hypothesis of the intervention of such a metastable intermediate in the reaction of azoxybenzene (19, 20).

If the overall process shown in Scheme 1 were in fact to occur this would constitute the first example of alkyl migration in the Wallach rearrangement. On the other hand it was tempting to conceive of the possibility that, in the absence of group migration, **3** would be stabilized in these media and thus become spectrally observable or otherwise lead to some product characteristic of that species.



SCHEME 1

Examination of **1** in strong sulfuric acid solutions (75–95% H_2SO_4) shows rather quickly that some kind of reaction does occur, since the spectrum characteristic of the protonated reactant disappears with time and is replaced by a new absorption which is stable in these reaction media (21). However, it was apparent that the reaction product was not phenolic since the spectrum of the base-quenched reaction mixture was qualitatively quite similar to the spectrum of the neutral or slightly acidic solution of the reaction product. This contrasts with the situation for azoxybenzene where the azophenolate ion was found to have its principal absorption displaced to longer wavelengths compared to the azophenol (19). To remove any possible doubt that **4** could have been formed from **1**, the authentic **4** was examined spectrally and found to have different characteristics in acidic and basic media. Similarly, 2,2′,4,4′,6,6′-hexamethylazobenzene, **5**, which could conceivably have been formed from **1** by reduction (by analogy with the reported (22) reduction of hexabromoazoxybenzene in strong acid) was found to have different spectral properties than the reaction product.



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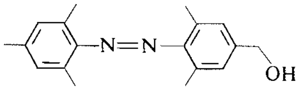


6

Since the reaction product did not appear to be a known compound, its isolation and physical characterization was deemed necessary. Product isolation was effected by treatment of a 6×10^{-4} M solution in 85.6% H_2SO_4 at 44.4° for 1 h (a concurrent spectral examination showed reaction to be complete) and work-up. A red crystalline solid was obtained whose u.v.-visible spectral characteristics corresponded to those of the species produced in the reaction as followed spectrophotometrically. The complete u.v. spectral data for the product as well as the reference compounds **1**, **4**, and **5** are given in Table 3, in neutral, acidic, and basic media. Some spectra in acid medium are shown in Fig. 1.

Elemental analysis of the reaction product showed it to be an isomer of the reactant. The i.r. spectrum showed pronounced absorption due to OH, pointing to an alcoholic material, since it is known not to be a phenol. In the n.m.r. spectrum, a 2-proton signal at 4.52 p.p.m. was indicative of the $ArCH_2OH$ grouping, in accord with structure **6**, and the rest of the n.m.r. spectrum was in complete agreement with that assignment. The presence of two distinct 2-proton peaks in the aromatic region shows that the CH_2OH function could not be present in an

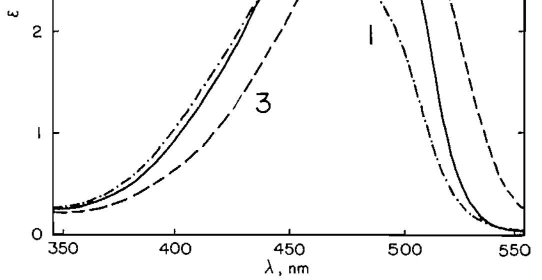
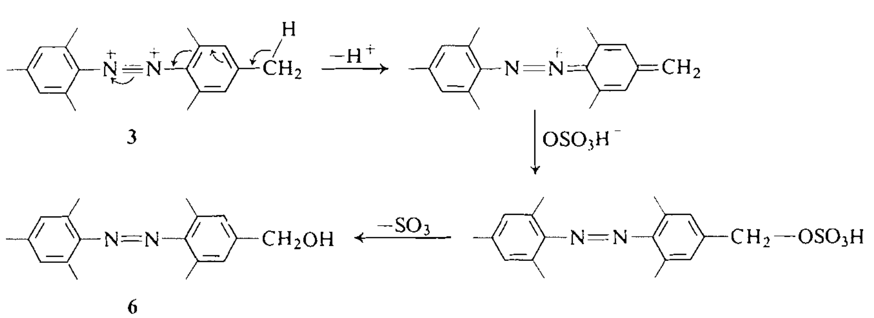


FIG. 1. Visible spectra in 87% H_2SO_4 of the reaction product **6** (curve 1), the azo-compound **5** (curve 2), and the phenol **4** (curve 3).

TABLE 3. Spectral data of the reaction product (**6**) and of the compounds **1**, **4**, and **5** in neutral, acidic, and basic media

Compound	Neutral^{a,b}		Acidic^{a,c}		Basic^{a,d}	
1	240	(7 500)	—		240	(7 500)
	306.5	(3 800)	387	(4 700)	307	(3 800)
5	237	(9 250)	252	(4 200)	237	(8 900)
	324	(14 800)	315	(2 500)	324	(14 400)
	462	(950)	475	(35 100)	462	(950)
4	249	(9 800)	258	(5 600)	264	(8 700)
	340	(15 200)	312	(2 800)	379	(18 800)
	463	(1 340)	488	(32 900)	—	
6	235	(8 500)	245	(4 200)	236	(7 900)
	321.5	(12 800)	312	(3 000)	320.5	(11 500)
	461	(1 050)	462.5	(28 400)	~450	(~850)

[a] λ in nm, (ε).
[b] In methanol, 8.00×10^{-5} *M*, in 1 cm cells.
[c] In 85.58% H_2SO_4, 4.00×10^{-5} *M*, in 1 cm cells.
[d] In 0.05 *M* KOH in methanol, 8.00×10^{-5} *M*, in 1 cm cells.



SCHEME 2

ortho position since in that case three aromatic signals should have been present in the ratio 2:1:1. Acetylation of the product resulted in loss of the O—H absorption and the appearance of a C=O peak in the i.r., while the n.m.r. spectrum showed the presence of a CH_3CO signal as well as a shift of the $ArCH_2O$ signal down-field by 0.4 p.p.m. from that of the reactant. The mass spectra of the reaction product and of the acetyl derivative were fully characteristic of the structural assignment given, *viz.* **6** for the reaction product and **6**-acetate for the derivative.

The unusual course of rearrangement of the substrate **1** could arise as a result of the reaction pathway indicated in Scheme 2, starting from the dicationic intermediate **3** which would be formed as previously (20). It should be pointed out that other pathways leading to product **6** are possible, for instance by direct nucleophilic attack by H_2O or HSO_4^- on a proton of the para methyl group of the conjugate acid **2**. However, the recent demonstration by Olah *et al.* that a dicationic species is formed from azoxybenzene in superacid (23) tends to lend support to the dicationic intermediate postulated in Scheme 2. Finally, we wish to draw attention to the synthetic potential of this reaction since nucleophilic substitution on methyls attached to aromatic rings is quite uncommon (24, 25).

Experimental

2,2′,4,4′,6,6′-Hexamethylazoxybenzene (1)

This compound was prepared by the peracid oxidation of 2,2′,4,4′,6,6′-hexamethylazobenzene (26). The azobenzene (6.66 g, 0.025 mol) was dissolved in chloroform (50 ml) in a 100 ml flask fitted with a reflux condenser and drying tube. *m*-Chloroperbenzoic acid (5.33 g, 0.026 mol, 85% Aldrich technical grade) was then added, and the solution refluxed on a steam-bath until it was a clear lemon-yellow color (4 h). The solution was cooled, washed with bicarbonate and water, and dried over calcium chloride. Rotary evaporation of the chloroform gave the product as a yellow oil which slowly crystallized into an amorphous yellow solid. Two recrystallizations from ethanol resulted in a crystalline solid (yellow plates); yield 84%, m.p. 63–64°.

Anal. Calcd. for $C_{18}H_{22}N_2O$: C, 76.56; H, 7.85; N, 9.92. Found: C, 76.87; H, 7.65; N, 10.07.

U.v. spectrum, see Table 1; n.m.r. δ 2.19 (s, 6, 2′- and 6′-CH_3); 2.30 (s, 3, 4-CH_3); 2.32 (s, 3, 4′-CH_3); 2.36 (s, 6, 2- and 6-CH_3); 6.79 (s, 2, 3- and 5-H); 6.84 (s, 2, 3′- and 5′-H).

4-Hydroxy-2,2′3,4′,6,6′-hexamethylazobenzene (4)

This substance was prepared by a standard diazo-coupling procedure (27), from 2,4,6-trimethylaniline and 2,3,5-trimethylphenol. Recrystallization from 60–80 petroleum ether gave the product as small red needles, m.p. 117–118°.

Anal. Calcd. for $C_{18}H_{22}N_2O$: C, 76.56; H, 7.85; N, 9.92. Found: C, 76.16; H, 7.68; N, 9.73.

U.v. spectrum, see Table 3; n.m.r. δ 2.16 (s, ~3, 3-CH_3); 2.28 (s, ~3, 4′-CH_3); 2.33 (s, ~6, 2′- and 6′-CH_3); 2.36 (s, ~6, 2- and 6-CH_3); 4.80 (broad, 1, OH); 6.26 (s, 1, 5-H); 6.78 (s, 2, 3′- and 5′-H).

4-Hydroxymethyl-2,2′,4′,6,6′-pentamethylazobenzene (6): Reaction Product Isolation

Hexamethylazoxybenzene (103.5 mg) was dissolved in 85.6% sulfuric acid (600 ml) in a 1 l flask which was heated in an oil-bath at 44.4° while stirring. A small portion of this solution was continuously scanned in the SP 800 spectrophotometer, using a 1 mm cell in a thermostatted cell block. When the scanned sample indicated that reaction was complete (1 h, 10 half-lives) the main reaction solution was cooled in ice. A portion of the reaction solution was quenched in 1 *M* NaOH in EtOH–H_2O (20:80) for spectral examination. The acidic reaction solution was then carefully diluted to 1200 ml with cold water and cooled again. The diluted acid solution was added slowly with continuous stirring and cooling to a solution of 750 g NaOH in 2 l water in a 20 l flask. Additional water had to be added to keep the Na_2SO_4 in solution and the final volume was about 10 l. This solution, which was cloudy with precipitated product, was extracted with small portions of ether until the aqueous layer was quite clear. The combined ether extracts were washed with water and dried over calcium chloride. Rotary evaporation of the ether left a red solid; the yield at this stage was 94.7 mg, or 91.5% of starting material. Purification was achieved by chromatography over neutral alumina, eluting with ether, and recrystallization from CCl_4. A mat of very fine red needles was obtained, m.p. 94–95°.

Anal. Calcd. for $C_{18}H_{22}N_2O$: C, 76.56; H, 7.85; N, 9.92. Found: C, 76.56; H, 7.85; N, 10.01.

U.v. spectrum, see Table 3; n.m.r. δ 2.32 (s, ~3, 4′-CH_3); 2.39 (s, ~12, 2-, 2′-, 6-, and 6′-CH_3); ~3.4 (broad, 1, OH); 4.52 (s, 2, Ar-CH_2-O); 6.83 (s, 2, 3′- and 5′-H); 6.98 (s, 2, 3- and 5-H). I.r. (cm^{-1}) 3445 (broad, bonded OH); 3618 (sharp, free OH). Mass spectrum, *m/e* (relative intensity) 282 (48), molecular ion; 135 (59), $C_6H_2(CH_3)_2CH_2OH^{\cdot +}$; 119 (100), $C_6H_2(CH_3)_3^{\cdot +}$; otherwise characteristic of an azo-compound (28).

4-Acetoxymethyl-2,2′,4′,6,6′-pentamethylazobenzene

The reaction product **6** was acetylated by refluxing it overnight in acetic acid – acetic anhydride (50:50). Rotary evaporation gave a red solid which was purified by column chromatography over acid-washed alumina, eluting with benzene – 60–80 petroleum ether (50:50), and recrystallization from ethanol. The product was a red crystalline solid, m.p. 65–66°.

Anal. Calcd. for $C_{20}H_{24}N_2O_2$: C, 74.05; H, 7.46; N, 8.63. Found: C, 74.27; H, 7.58; N, 8.63.

U.v. (CH_3OH) λ 239 nm (ε 8700); 317 (12 400); 458 (1040). N.m.r. δ 2.01 (s, 3, CH_3—C=O); 2.27 (s, 3, 4′-CH_3); 2.40 (s, 12, 2-, 2′-, 6-, and 6′-CH_3); 4.94 (s, 2, Ar-CH_2-O); 6.82 (s, 2, 3′- and 5′-H); 7.00 (s, 2, 3- and 5-H). I.r. (cm^{-1}) 1730 (C=O). Mass spectrum, *m/e* (relative intensity) 324 (52), molecular ion; 177 (19), $C_6H_2(CH_3)_2CH_2OCOCH_3^{\cdot +}$; 119 (100), $C_6H_2(CH_3)_3^{\cdot +}$; 220 (23); otherwise typical of an azo-compound (28).

Spectral Measurements

The u.v.-visible spectral measurements were performed by the method previously described (10). The n.m.r. spectra were taken on a Varian T60 instrument, in CCl_4 solution, and the data are quoted as p.p.m. relative to TMS internal standard. The i.r. spectra were obtained in $CHCl_3$ solution using a Unicam SP 1000 spectrophotometer.

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