The Nature of the Internal Hydrogen Bond. Part II. Electronic Spectra of 2-Nitrosoanisole and 6-Methoxyiminocyclohexa-2 : 4-dienone (o-Benzoquinone 1-Monoxime Methyl Ether) and their Derivatives.*

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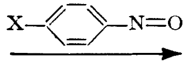
The spectra of nitrosobenzene, 2-nitrosoanisole and its 5-methoxy- and 5-dimethylamino-derivatives, and 6-methoxyimino*cyclo*hexa-2 : 4-dienone and its 3-methoxy- and 3-dimethylamino-derivatives in a series of solvents are analysed. A qualitative interpretation of the electronic transition responsible for *B*-bands is given.

Investigation of the electronic spectra of organic molecules has established that there are two principal types of absorption bands above 2000 Å (*R*- and *K*-bands) which are distinguished by different intensities (ε <2000 and >5000, respectively) and optical rules (Burawoy, *Ber.*, 1930, **63**, 3155; 1931, **64**, 464, 1635; 1932, **65**, 941; *J.*, 1937, 1865; 1939, 1177; *Discuss. Faraday Soc.*, 1950, **9**, 70; Burawoy and Spinner, *J.*, 1955, 2557; cf. also Gillam and Stern, " Electronic Absorption Spectroscopy in Organic Chemistry," Edward Arnold and Co., London, 1954, p. 111).

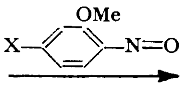
Although the characteristic long-wave benzenoid bands observed in the spectra of benzene and many aromatic compounds possess lower intensities (ε generally less than 5000) and superficially appear to obey different rules, they originate in electronic transitions of the same type as those responsible for the *K*-bands (cf. below). Following a suggestion by Braude (*Ann. Reports*, 1945, **42**, 105) these bands will be referred to as *B*-bands.

We have examined the electronic spectra of 2-nitrosoanisole, 6-methoxyimino*cyclo*hexa-2 : 4-dienone (*o*-benzoquinone 1-monoxime methyl ether), and a few of their derivatives, since the qualitative understanding of these was required for the investigation of the structure of 2-nitrosophenols to be discussed in Part III (following paper).

The spectrum of nitrosobenzene (Fig. 1) in ethyl alcohol shows two types of absorption band above 2200 Å : (i) A *K*-band system of comparatively high intensity, consisting of two peaks at 2815 and 3055 Å (ε 9500 and 7000, respectively), which originates in a transition involving an electron migration along the conjugated system as indicated in (I) and corresponds to the benzene band at 2000 Å and the weak ethylene band system in the 1700 Å region. (ii) An *R*-band of low intensity at 7560 Å (ε 45), characteristic of the nitroso-group. The band corresponding to the 2600 Å band system of benzene is not observed since it is masked by the *K*-band absorption of higher intensity.

(I) 

(X = H, OMe, or NMe$_2$)

 (II)

K-*Bands*.—The *K*-band of nitrosobenzene is displaced to longer wave-lengths in the spectra of 4-nitrosoanisole and *NN*-dimethyl-4-nitrosoaniline (Table 1). A similar red-shift of the *K*-band is observed in the series, 2-nitrosoanisole, 2 : 4-dimethoxy-1-nitrosobenzene, and 5-dimethylamino-2-nitrosoanisole (cf. Fig. 1 and Table 1). The methoxy- and dimethylamino-groups in the *para*-position to the nitroso-group are terminal groups of the absorbing conjugated system (I or II) and thus increase the polarity of the system as well as its length, *i.e.*, the electronic polarisability of the terminal group (cf. Burawoy and Spinner, *loc. cit.*). In contrast, a methoxy-group *ortho* to the nitroso-group, *i.e.*, in a branch of the absorbing conjugated system, does not increase the length of the system and modifies only slightly its polarity and thus has a smaller (bathochromic) effect on the *K*-band (for the spectra of nitrosobenzene and 2-nitrosoanisole, see Fig. 1, and for the data of all three investigated pairs of compounds, see Table 1).

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* Part I, *J.*, 1952, 4793.

B-*Bands.*—In contrast to the *K*-band, the (masked) *B*-band of nitrosobenzene is strongly displaced to longer wavelengths, with an increased intensity, by an *ortho*-methoxy-group. It appears in the spectrum of 2-nitrosoanisole at 3770 Å (ε 4800), but remains masked in the spectra of 5-methoxy- and 5-dimethylamino-2-nitrosoanisole because of the red-shift of the *K*-band caused by the *para*-substituent. Moreover, a comparison of the spectra of 2-nitrosoanisole and its 5-methoxy-derivative (Fig. 1) shows that a *para*-methoxy-group can have only a small (probably hypsochromic) effect on the *B*-band. This reversed effect on the *K*- and *B*-bands, respectively, of a methoxy-group in *ortho* and the *para*-position to the nitroso-group is most characteristic and is also observed in the spectra of the corresponding hydroxy-derivatives of azobenzene, nitrobenzene, benzaldehyde, and diphenyl (for data, cf. Burawoy and Chamberlain, *J.*, 1952, 2310, 3734). Substituents such as amino and mercapto behave similarly, as shown in Table 2 by the spectra of the corresponding nitrobenzene derivatives.

TABLE 1. *Spectra of nitrosobenzene derivatives, in ethanol.*

	R-Band		*B*-Band		*K*-Band	
Compound	$\lambda_{max.}$ (Å)	ε	$\lambda_{max.}$ (Å)	ε	$\lambda_{max.}$ (Å)	ε
C_6H_5·N:O	7560	45	—	—	2815 3055	9500 7000
1 : 2-MeO·C_6H_4·N:O	7610	41	3770	4800	2880 3090	6900 5600
1 : 4-MeO·C_6H_4·N:O	7275	47	—	—	3455	11,600
2 : 4 : 1-$(MeO)_2C_6H_3$·N:O	7250	48	—	—	3690	12,100
1 : 4-Me_2N·C_6H_4·N:O	6740	55	—	—	4200	30,400
2 : 4 : 1-MeO·$C_6H_3(NMe_2)$·N:O	6560	62	—	—	4210	33,800

FIG. 1.

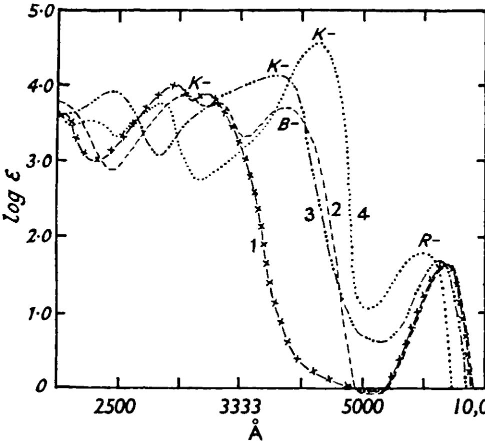


FIG. 2.

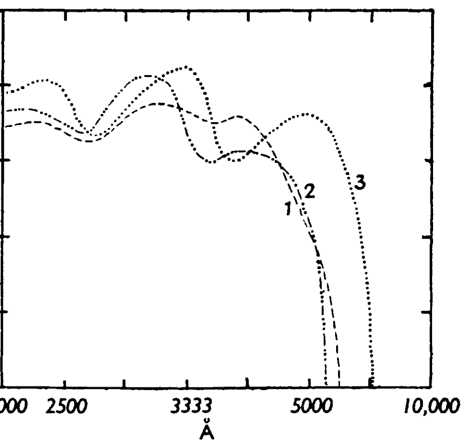


FIG. 1. 1, *Nitrobenzene.* 2, 2-*Nitrosoanisole.* 3, 2 : 4-*Dimethoxy*-1-*nitrosobenzene.* 4, 5-*Dimethylamino*-2-*nitrosoanisole.* In ethanol.

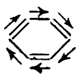
FIG. 2. 1, 6-*Methoxyimino*cyclo*hexa*-2 : 4-*dienone.* 2, 3-*Methoxy*-6-*methoxyimino*cyclo*hexa*-2 : 4-*dienone.* 3, 3-*Dimethylamino*-6-*methoxyimino*cyclo*hexa*-2 : 4-*dienone.* In ethanol.

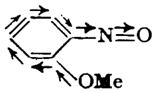
TABLE 2. *Spectra of nitrobenzenes,* X·C_6H_4·NO_2, *in ethanol.*

X		H	2-NH_2	4-NH_2	2-OH	4-OH	2-SH	4-SH
B-Band	$\lambda_{max.}$ (Å)	—	4030	—	3435	—	3540	—
	ε	—	6100	—	3600	—	3700	—
K-Band	$\lambda_{max.}$ (Å)	2595	2777	3725	2730	3140	2705	3175
	ε	9500	4900	16,800	6600	13,000	5700	24,000

These observations throw light on the nature of the electronic transition responsible for the *B*-bands; they suggest that the *B*-bands originate in the same type of electronic transition as the *K*-bands, but correspond to electronic migrations along the conjugated system formed by all three benzene double bonds as indicated for benzene and 2-nitrosoanisole in formulæ (III) and (IV). Substituents such as hydroxy, amino, and mercapto *ortho* to double-bond groups are now terminal groups of the absorbing system and responsible for appreciable red-shifts, whereas in the *para*-position they are in a side-chain and have much smaller effects. Moreover, since the transition moment is much smaller, or even negligible, the lower intensities of the *B*-bands compared with those of the *K*-bands are also accounted for. This qualitative interpretation will be extended by a more detailed and fundamental discussion elsewhere.

(III)





(IV)

R-*Bands*.—The effect of the methoxy- and the dimethylamino-group on the *R*-band of the nitroso-group is again different. The band is displaced to shorter wavelengths by the introduction of these groups in the *para*-position, the more strongly electron-repelling dimethylamino-group causing the greater blue-shift. The effect of an *ortho*-methoxy-group is small, a slight red-shift being observed in 2-nitrosoanisole (cf. Fig 1 and Table 1), very little change in 2 : 4-dimethoxy-1-nitrosobenzene, and a moderate blue-shift in 5-dimethylamino-2-nitrosoanisole (cf. Table 1). As already shown (Burawoy, *loc. cit.*, 1939), direct substitution of the nitroso-group by these substituents, *e.g.*, in the yellowish alkyl nitrites (λ 3570 Å; ε 75) and dimethylnitrosamine (λ 3435 Å; ε 97), is responsible for even greater displacements of the *R*-band to shorter wavelengths. As far as investigated, these effects are characteristic of the *R*-bands of all double bonds, *e.g.*, those of the N:N, C:S, and C:O groups (Burawoy, *locc. cit.*, 1930, 1937, 1939).

Solvent Effect.—Data showing the effect of solvents on the spectra of nitrosobenzene (I; X = H) and of 2-nitrosoanisole (II; X = H) and its 5-methoxy- (II; X = OMe) and 5-dimethylamino-derivatives (II ; X = NMe_2) are summarised in Table 3. This effect is undoubtedly complex, being dependent on the nature of the electronic transition (type of band) and the various possible solute–solvent interactions (for a discussion of the principles involved, cf. Bayliss and McRae, *J. Phys. Chem.*, 1954, **58**, 1002, 1006).

The data are in agreement with the following earlier conclusions (Burawoy, *locc. cit.*; in particular 1930, 1937, 1939, 1950) : (i) The *K*-bands (and *B*-bands) are displaced to longer, and the *R*-bands to shorter wavelengths approximately in the order of the increasing dielectric constant of the solvent: $C_6H_{14} < CCl_4 \sim Et_2O < C_6H_6 < CHCl_3 \sim EtOH < H_2O$. This is due mainly to the increasing polarity of the absorbing system in the ground state. The polarisability of the solvent (as indicated by its refractive index alone), the importance of which has been emphasised by Bayliss and his collaborators (*loc. cit.*, cf. also *J. Chem. Phys.*, 1950, **18**, 292), should make a smaller contribution in the case of the polar molecules and simple solvents investigated. The different effect of solvents on *R*- and *K*-bands (interpreted to correspond to $n \longrightarrow \pi$ and $\pi \longrightarrow \pi$ transitions) has been recently discussed by McConnell (*J. Chem. Phys.*, 1952, **20**, 700). (ii) The increase in the polarity due to the solute–solvent interaction, and thus the magnitude of the solvent effect is enhanced with the polar character of the absorbing molecules. It is small for nitrosobenzene and 2-nitrosoanisole, moderate for the 5-methoxy-derivative, and appreciable for 5-dimethylamino-2-nitrosoanisole.

Whereas the *K*-bands are usually at the longest wavelengths in water, that of *NN*-dimethyl-3-methoxy-4-nitrosoaniline (II; X = NMe_2) appears at shorter wavelengths (4160 Å) in this solvent than in chloroform (4180 Å) and ethanol (4210 Å). This partial reversal of the normal solvent effect may be attributed to the formation of an external hydrogen bond by the dimethylamino-group. This is similar to the behaviour of dimethylaniline itself as explained by Ungnade (*J. Amer. Chem. Soc.*, 1953, **75**, 432). Both the *B*- and *K*-bands of dimethylaniline are displaced to shorter wavelengths in passing from *cyclo*hexane or ethyl alcohol (λ 2980 and 2510 Å respectively; log ε 3·37 and 4·16) to water (λ 2840 and 2440 Å; log ε 3·11 and 3·94). This effect is too big to be attributed to the smaller polarisability of water, as suggested by Bayliss and McCrae (*loc. cit.*).

TABLE 3. *Effect of solvents on the spectra of nitrosobenzenes* (I *and* II).

		(I; X = H)		(II; X = H)		(II; X = OMe)		(II; X = NMe_2)	
Solvent	Band	$\lambda_{max.}$ (Å)	ε	$\lambda_{max.}$ (Å)	ε	$\lambda_{max.}$ (Å)	ε	$\lambda_{max.}$ (Å)	ε
C_6H_{14}	*R*	7660	45	—	—	—	—	—	—
	K	2800	11,900	—	—	—	—	—	—
		3025	5900						
Et_2O	*R*	7625	44	7770	46	7525	50	—	—
	B	—	—	3715	4950	—	—	—	—
	K	2810	7650	2870	6900	3610	11,250	4000	30,300
		3035	4900	3060 *	3700				
CCl_4	*R*	—	—	7770	53	—	—	7340	68
	B	—	—	3690	4850	—	—	—	—
	K	—	—	2890	5750	3605	11,200	4015	30,200
				3040 *	3750				
C_6H_6	*R*	7640	48	7760	54	7475	59	7310	72
	B	—	—	3755	4600	—	—	—	—
	K	2835	9250	2895	6300	3660	10,800	4070	28,700
		3070	7800	3060 *	4300				
$CHCl_3$ ...	*R*	7550	48	7660	49	7360	56	7080	76
	B	—	—	3800	4800	—	—	—	—
	K	2835	11,800	2890	6600	3710	12,100	4180	35,000
		3055	10,600	3090	5400				
EtOH ...	*R*	7560	45	7610	41	7250	48	6560	62
	B	—	—	3770	4800	—	—	—	—
	K	2815	9500	2880	6900	3690	12,100	4210	33,800
		3055	7000	3090	5600				
H_2O	*R*	7310	29	7440 †	23	6990 †	54	5450 *	123
	B	—	—	3910	2700	—	—	—	—
	K	2825	6250	2860	5300	3740	12,200	4160	28,500
		3065	8500	3120	5650				
D ‡	*R*	− 65 Å		−160		−275		− 780	
		−120 cm.$^{-1}$		−270		−500		−1620	
	B	—		+ 55		—		—	
				+400					
	K	+ 10 Å		+ 20		+ 80		+ 210	
		+130 cm.$^{-1}$		+250		+600		+1250	

* Inflexion. † Ethanol–water (1 : 1).

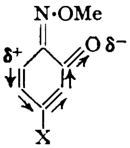
‡ Displacement *D*($Et_2O \longrightarrow$ EtOH), except for *R*-band in (II; X = NMe_2), which is *D*($CCl_4 \longrightarrow$ EtOH).

6-Methoxyiminocyclohexa-2 : 4-dienones (*o-Benzoquinone 1-Oxime Methyl Ethers*).— A detailed and unambiguous analysis of the spectra of 6-methoxyimino*cyclo*hexa-2 : 4-dienone (V; X = H) and its 3-methoxy- (V; X = OMe) and 3-dimethylamino-derivatives (V; X = NMe_2) (for data, cf. Fig. 2 and Table 4) would require an extensive knowledge of the *o*-benzoquinone system and will not be attempted. The following observations can, however, be made.

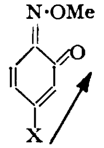
The spectra above 2500 Å of the three compounds in all solvents consist of two band systems, of which that at longer wavelengths possesses a lower intensity. No *R*-band is observed since the nitroso-group is absent and that of the carbonyl group masked by the more intense bands. The band system at shorter wavelengths (a *K*-band) of the parent compound in ethanol has one peak at 3070 Å (ε 5500) and an inflexion at 3350 Å (ε 4400). It is very similar to the *K*-band system of the isomeric 2-nitrosoanisole in ethanol (λ 2880 and 3090 Å; ε 6900 and 5600) in spite of the very different structures of the two compounds.

The corresponding *K*-bands of the 3-methoxy- and 3-dimethylamino-derivatives in ethanol consist of only one peak of higher intensity, but, in contrast to the isomeric 2-nitrosoanisoles, the introduction of these groups has only a small effect on the position of the peak, the methoxy-group displacing to shorter and the dimethylamino-group to longer wavelengths (−60 and +220 Å, respectively). Since these groups behave as if present in a side-chain of the absorbing (conjugated) system, the electron transition may involve an electron migration as indicated in (V).

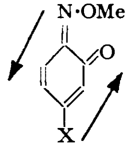
Again, both the intensity and position of the long-wave band in the spectrum of the parent methoxyiminocyclohexadienone (λ 3780 Å; ε 3800) and of the *B*-band in the spectrum of 2-nitrosoanisole (λ 3770 Å; ε 4800) are very similar. However. in contrast to 5-methoxy- and 5-dimethylamino-2-nitrosoanisole, this band appears in the spectra of the 3-methoxy- and 3-dimethylamino-6-methoxyiminocyclohexadienone at 4010 and 4890 Å, respectively (in ethanol), *i.e.*, red-shifts of 230 and 1110 Å being observed. This allows little doubt that the methoxy- and dimethylamino-groups are terminal groups of the absorbing conjugated system and indicates the electronic transition shown in (VI).



(V)



(VI)



(VII)

This would not account for the only moderate intensities (ε 1550 and 4000, respectively) which correspond to those of *B*-bands. It may, therefore, be suggested that the electron migration involved in the transition is coupled with one in the opposite direction as indicated in (VII), resulting in the small transition moment characteristic of *B*-bands.

Data for the effect of solvents on the bands of all three methoxyiminocyclohexadienones are summarised in Table 4. As in the case of the *B*- and the *K*-bands of the 2-nitrosoanisoles, moderate red-shifts, approximately in the order of solvents, $Et_2O \sim CCl_4 < C_6H_6 < CHCl_3 \sim EtOH < H_2O$, are observed, the displacements being smallest in the case of the least polar parent methoxyiminocyclohexadienone. Again, the formation of an external hydrogen bond with water should account for the blue-shift of the *B*-band and rather small red-shift of the *K*-band of the 3-dimethylamino-derivative in this solvent as compared with their positions in chloroform and ethanol.

TABLE 4. *Effect of solvents on the spectra of* 6-*methoxyimino*cyclo*hexa*-2 : 4-*dienones* (V).

		(V; X = H)		(V; X = OMe)		(V; X = NMe$_2$)	
Solvent	Band	$\lambda_{max.}$ (Å)	ε	$\lambda_{max.}$ (Å)	ε	$\lambda_{max.}$ (Å)	ε
Et_2O	*B*	3750	3600	3760	1950	4700	2600
	K	3030	4800	2940	13,300	3160	14,700
		3320 *	3700			3290	13,600
CCl_4	*B*	3700	4000	3880	2300	4770	2750
	K	3050	4300	2985	16,600	3215	14,100
		3350	4000				
C_6H_6	*B*	3740	4000	3920	1700	4810	3100
	K	3060	5050	3010	15,400	3235	16,400
		3350	4100				
$CHCl_3$	*B*	3830	3200	3960	1750	4890	3750
	K	3060	4750	3010	12,200	3275	16,300
		3350 *	3400				
EtOH	*B*	3780	3750	4010	1550	4890	4000
	K	3070	5550	3010	14,900	3290	16,700
		3325 *	4400				
H_2O	*B*	3910	3000	4110	1750	4830	5000
	K	3080	5600	3060	13,200	3310	18,900
		3350 *	4400				
D †	*B*	+30 Å		+250		+190	
	K	+25		+ 70		+ 65	

* Inflexion. † $D(Et_2O \longrightarrow EtOH)$.

EXPERIMENTAL

Spectra of the nitroso-compounds and 6-methoxyiminocyclohexadienones were determined with a Hilger Uvispek Photoelectric Spectrophotometer. The concentrations used varied between 0·01M and 0·0025M for the *R*-bands and between 0·0001M and 0·0004M for the *B*- and *K*-bands. The data for the nitrobenzene derivatives (Table 2) are new determinations carried out with a Hilger E3 quartz spectrograph fitted with a Spekker photometer, a tungsten-steel high-tension spark being employed as the source of light; those for nitrobenzene and the nitrophenols have already been reported (Burawoy and Chamberlain, *loc. cit.*).

Materials.—2-*Nitrosoanisole.* This formed white plates (from water), m. p. 103° (Baeyer and Knorr, *Ber.*, 1902, **35**, 3036, give m. p. 103°).

6-*Methoxyimino*cyclo*hexa*-2 : 4-*dienone.* Aqueous silver nitrate (3·5 g. in 20 c.c.) was added to aqueous sodium 2-nitrosophenoxide (Baeyer and Knorr, *loc. cit.*; 3 g. in 20 c.c.), and the silver 2-nitrosophenoxide filtered off. Methyl iodide (10 g.) was shaken with a suspension of the dry silver salt in dry ether (200 c.c.) for 50 hr., the resulting ethereal solution filtered, the ether removed under reduced pressure, and the residue (1 g.; 35%) crystallised from light petroleum (b. p. 40—60°). The *methoxyimino*cyclo*hexadienone* formed orange needles, m. p. 48° (Found: C, 61·1; H, 4·8; N, 10·2. $C_7H_7O_2N$ requires C, 61·3; H, 5·1; N, 10·2%).

2 : 4-*Dimethoxy*-1-*nitrosobenzene.* Attempts to prepare this compound by the action of sodium nitrite on resorcinol dimethyl ether in presence of aqueous mineral acid failed, nitrosation being accompanied by demethylation. It was obtained by the following methods: (i) Potassium persulphate (5·7 g.) was gradually added to concentrated sulphuric acid (9 c.c.) with stirring, the temperature being kept below 15°. The mixture was stirred for another 45 min. and then poured on ice (200 g.). The solution was neutralised with potassium carbonate and finally made slightly acidic with dilute acetic acid, the temperature being kept at 0—5°. 2 : 4-Dimethoxyanilinium chloride (1·8 g.) in water (150 c.c.) was neutralised with sodium hydroxide and slightly acidified with dilute acetic acid. The solution of Caro's acid was added at once, the temperature being kept below 5°. After 30 min., salt was added and the precipitate collected and steam-distilled. 2 : 4-*Dimethoxy*-1-*nitrosobenzene* (0·6 g., 45%) was again salted out and crystallised from water or light petroleum, forming green needles, m. p. 98—99° (Found: C, 57·6; H, 5·5; N, 8·6. $C_8H_9O_3N$ requires C, 57·5; H, 5·4; N, 8·4%). (ii) Sodium nitrite (6·9 g.) was added slowly to concentrated sulphuric acid (69 c.c.) with stirring and cooling below 10°. The temperature was slowly raised to 65°, a clear solution being obtained. Resorcinol dimethyl ether (4·6 g.) was added dropwise, the temperature being maintained below 5°; stirring was continued for another 15 min. and the mixture poured on to ice water and sodium carbonate. The precipitate (4·1 g., 73%) was crystallised from light petroleum, giving green needles, m. p. 98—99°, identical with the product obtained from dimethoxyanilinium chloride.

3-*Methoxy*-6-*methoxyimino*cyclo*hexa*-2 : 4-*dienone.* This formed orange spears (from light petroleum), m. p. 115—116° (Henrich and Eisenach, *J. prakt. Chem.*, 1904, **70**, 332, give m. p. 115—117°).

5-*Dimethylamino*-2-*nitrosoanisole.* This was obtained as green needles (from carbon tetrachloride), m. p. 131° (Fieser and Thompson, *J. Amer. Chem. Soc.*, 1939, **61**, 382, give 131°).

3-*Dimethylamino*-6-*methoxyimino*cyclo*hexa*-2 : 4-*dienone.* Aqueous silver nitrate (6 g. in 30 c.c.) was added to 5-dimethylamino-2-nitrosophenol (5 g.) in water (180 c.c.) and sodium hydroxide (15 c.c.; 2N). The dried silver salt was shaken with methyl iodide (5 g.) in dry ether (350 c.c.) in a stoppered bottle for 48 hr. The solution was filtered, the ether removed and the 3-*dimethylamino*-6-*methoxyimino*cyclo*hexadienone* (4 g., 74%) crystallised from carbon tetrachloride, giving reddish-brown needles, m. p. 149°. The product is easily soluble in water and is very hygroscopic (Found: C, 59·6; H, 6·6; OMe, 17·6. $C_9H_{12}O_2N_2$ requires C, 60·0; H, 6·7; OMe, 17·2%).

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