Tetrahedron Letters No.20, pp 1433-1436, 1965. Pergamon Press Ltd.
Printed in Great Britain.

OXIDATION WITH NICKEL PEROXIDE. V. (1)
THE FORMATION OF cis,cis-1,4-DICYANO-1,3-BUTADIENES IN THE OXIDATION OF o-PHENYLENDIAMINES

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(Received 24 March 1965)

In the course of our works on the oxidation with nickel peroxide, we observed that benzylamines and alkyl amines were easily oxidized in benzene solution to give the corresponding nitriles in good yields, and that catechol was easily transformed into cis,cis-muconic acid in an aqueous alkaline solution with oxidative cleavage of benzene ring.

As an extension of the study of oxidative action of nickel peroxide, we carried out the oxidation of o-phenylendiamine.

To a solution of o-phenylendiamine in benzene or ether there was slowly added nickel peroxide with stirring at room temperature. The oxidation*[1] was conducted by employing two times the theoretical amounts of nickel peroxide based on the available oxygen-content which was determined by iodometry. The reaction proceeded very

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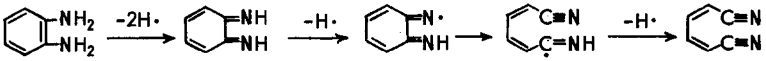
*[1] The mechanism of oxidation may be suggested as follows:



rapidly and the colour of the solution was turned into red-brown. After removal of nickel peroxide, the filtrate was concentrated and the solution was chromatographed on alumina. *cis,cis*-1,4-Dicyano-1,3-butadiene obtained from the first elute was recrystallized from carbon tetrachloride to give white crystals, m.p. 128-129°, (Anal. Calcd. for $C_6H_4N_2$: C, 69.21; H, 3.88; N, 26.91. Found: C, 69.12; H, 3.97; N, 26.64). Catalytic reduction of the product over platin oxide afforded adiponitrile with absorption of two moles of hydrogen.

The *cis,cis* configuration of the product was established by comparison of the infrared spectrum, ultraviolet spectrum, proton spin resonance and mixture melting point with an authentic *trans,trans* sample independently prepared from 1,4-dicyano-2-butene (2). The ultraviolet spectrum of the product in 95% ethanol showed the maximums at 260 mμ (ε 28,600) and 271 mμ (ε 21,200), but *trans,trans* isomer showed 259 mμ (ε 37,900) and 270 mμ (ε 31,200). The infrared spectrum in KBr tablet exibited the bands at 3065 cm^{-1} (=C-H stretching vib.), 2219 cm^{-1} (conjugated C N stretching vib.), 1608 cm^{-1} and 1555 cm^{-1} (C=C stretching vib., Raman and infrared) and also clearly demonstrated the presence of cisoid disubstituted carbon-carbon double bond at 756 cm^{-1} (CH=CH out of plane deform. vib.) On the other hand, trans,trans isomer showed the presence of transoid disubstituted carbon-carbon double bond at 985 cm^{-1}. The n.m.r. spectrum[*2] of *cis,cis* isomer (an A_2X_2 type) shows two protons of C_1 and C_2 at 4.25τ and two protons of C_2 and C_3 at 2.66τ. That of *trans,trans* isomer shows two protons of C_1 and C_4 at 4.26τ and two protons of C_2 and C_3 at 2.96 τ.

This reaction was successfully applied for some kinds of *o*-phenylendiamine derivatives as shown in Table I. The yields and physical properties of new compounds

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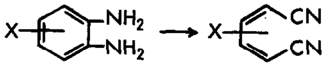
[*2] Spectra were determined in deuterochloroform at 60 Mc/sec with a Varian A·60 spectrometer using tetramethylsilane as internal reference.

TABLE



o-Phenylendiamine	Product[c] Yield (%)	m.p. (°C)[b]
o-Phenylendiamine a)	14.2	128 - 129
3-Methyl	8.2	70.5-71.0
4-Methyl	9.2	56.5-57.5
4,5-Dimethyl	13.4	107 - 108
3,4-Dimethyl	5.8	47 - 48
3,5-Dimethyl	7.2	55.5-56.0
3,6-Dimethyl	6.6	137 - 138
4-Methoxy	11.6	116 - 117
4-Chloro a)	6.1	89 - 90
4-Nitro	0	
4-Cyano	0	
1,2-Diaminonaphthalene	25.8	70.0-70.5
2,3-Diaminonaphthalene	0	

All oxidations were carried out in a solution of 2-3% reactant in ether.

a) Benzene was used instead of ether. b) Melting points are uncorrected. c) Satisfactory analyses were obtained for all new compounds described here.

obtained here were presented.

The dienophilic character of cis,cis-1,4-dicyano-1,3-butadiene was displayed by the formation of the Diels-Alder adduct, m.p. 100-101°, in the reaction with cyclopentadiene.

It is known (4) that the oxidation of o-phenylendiamine with ferric chloride gives diaminophenazine and with silver oxide or lead dioxide does o-quinone diimine. The different results obtained with nickel peroxide are quite interesting and under active investigation.

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