

The Stabilities of Meisenheimer Complexes. Part 28.¹ The Reactions of 2,2',4,4',6,6'-Hexanitrobibenzyl with Alkoxides

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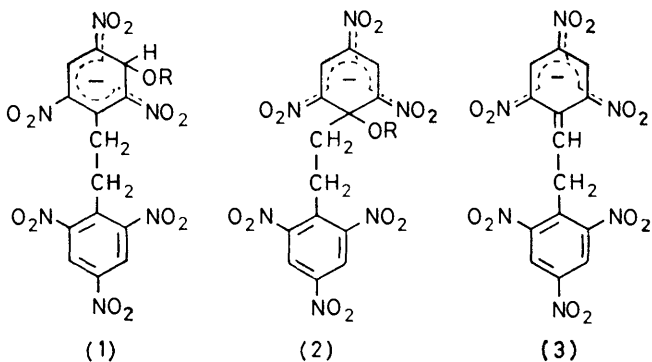
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¹H N.m.r. and visible spectral measurements indicate that in the presence of alkoxide ions 2,2',4,4',6,6'-hexanitrobibenzyl forms σ -adducts by base addition. Attack at the 3-(3'-) positions precedes attack at the 1-(1'-) positions but gives thermodynamically less stable adducts. Kinetic and equilibrium data are reported for the formation in ethanolic sodium ethoxide of 1 : 1 adducts by attack at the 3- or 1-position and for the formation of a 1 : 2 adduct by addition at the 1- and 1'-positions. Data are also reported for the formation in methanolic sodium methoxide of a 1 : 1 adduct formed by attack at the 1-position. These results are compared with values obtained for σ -adduct formation of related substrates.

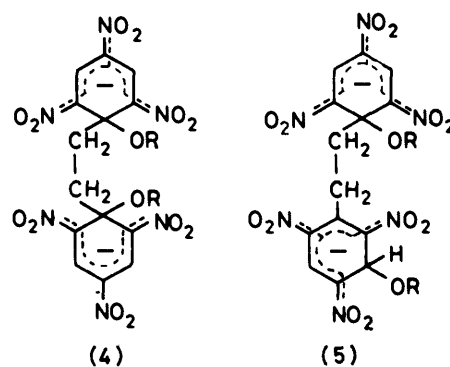
ONE method for the production of the commercially important product 2,2',4,4',6,6'-hexanitrostilbene is the dehydrogenation of 2,2',4,4',6,6'-hexanitrobibenzyl (HNBB) by quinones in basic media.^{2,3} Clearly a knowledge of the mode or modes of interaction of HNBB with base is important to the understanding of the mechanism of this reaction. We report here on the reversible reactions of HNBB with alkoxide ions.

By analogy with related compounds, such as 2,4,6-trinitrotoluene (TNT) and 2,4,6-trinitrobenzyl chloride (TNBCl),⁴ likely products of (1 : 1) interaction with base are the σ -adducts (1) or (2) formed by base attack at the 3- or 1-positions respectively, or the conjugate base (3). Because of the separation of the aromatic rings by two methylene groups it might be expected that dianionic species would readily be formed.



¹H N.m.r. Measurements.—The spectrum of the parent in [2H₆]dimethyl sulphoxide shows two singlets at δ 3.35 and 9.0 due respectively to methylene and ring protons. The addition of 2 mol. equiv. of sodium trideuteriomethoxide in [2H₄]methanol resulted in the rapid formation, at the expense of the ring proton band, of two doublets at δ 6.1 and 8.5. These bands decreased in intensity with time and two singlets at δ 8.53 and 8.6 were observed. The band at δ 8.53 eventually took all the intensity due to ring protons and the final spectrum, observed after 6 min † and stable over the next 10 min,

consisted of this band and a singlet of equal intensity at δ 2.40. This spectrum is consistent only with the diadduct (4) in which methoxide attack has occurred at the 1- and 1'-positions of the parent. The shift to high field, relative to the resonance positions of the parent, of the ring and methylene proton resonances is in agreement with similar shifts in related systems.⁵ The initial



observation of doublets at δ 6.1 and 8.5 indicates that methoxide attack at the unsubstituted 3- and/or 3'-positions occurs rapidly.⁵ Accordingly the spectrum of the parent in the presence of 1 mol. equiv. of base initially showed doublets at δ 6.1 and 8.5 and a broad band at δ 8.9 which may be attributed to the ring protons of (1; R = Me). The broadness of the band (δ 8.9) due to protons in the unattacked ring may indicate that some electron transfer to give radical anions occurs.⁵ The band at δ 8.6 observed at intermediate times in solutions containing 2 equiv. of base may be due to the ring protons in the 1-methoxy-ring of the diadduct (5) which will presumably be present as a transient species. A further possibility is that this band is due to a thermodynamically unfavourable rotational isomer of the diadduct (4).

The main conclusion from these measurements is that attack at unsubstituted ring positions is kinetically

† 1 min = 60 s.

favoured while attack at the 1- and 1'-positions leads to the thermodynamically more stable products.

Reaction with Sodium Methoxide in Methanol.—In the presence of dilute (<0.2M) sodium methoxide in methanol a rapid reversible reaction is observed giving a species with λ_{max} 430 and 500 nm (shoulder). This is followed fairly quickly (minutes) by irreversible decomposition of the substrate. Examination of the system by stopped flow spectrophotometry indicated that a single rapid colour-forming reaction was present. Data are in Table 1. These data are best interpreted as

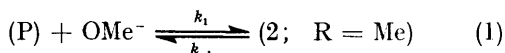
TABLE 1

Kinetic and equilibrium data for the reaction of 2,2',4,4',-6,6'-hexanitrobiphenyl with sodium methoxide in methanol at 25 °C *

[NaOMe]/M	$k_{\text{obs.}}/s^{-1}$	OD (480 nm) ^a	K_1 ^b /l mol ⁻¹
0.01	1.4 ± 0.1	0.0041	23
0.02	1.6	0.0066	21
0.04	2.1	0.0098	20
0.07	2.8	0.0114	16
0.10	3.4	0.0146	20

* °C = K - 273.15. ^a For 1×10^{-5} M parent measured with a 2 mm cell. A Benesi-Hildebrand plot gives a value of 0.022 for complete conversion, corresponding to a value for ϵ of 1.1×10^4 l mol⁻¹ cm⁻¹. ^b Calculated using the expression $OD(480)/[0.022 - OD(480)][NaOMe]$.

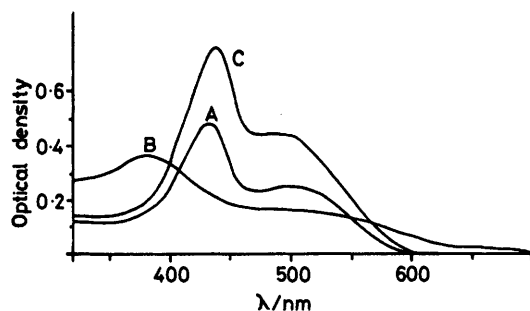
shown in equation (1) as reaction of the parent (P) with methoxide ions to give the adduct (2; R = Me). Since the base concentration is in large excess over the parent equation (2) will apply.



$$k_{\text{obs.}} = k_1[OMe^-] + k_{-1} \quad (2)$$

A linear plot of $k_{\text{obs.}}$ versus base concentration gave values for k_1 of 23 l mol⁻¹ s⁻¹ † and k_{-1} of 1.15 s⁻¹. Combination of these values gives a value for K_1 of 20 l mol⁻¹ in good agreement with that obtained from equilibrium optical density measurements.

The visible spectrum is consistent ^{4,5} with the formation of a σ -adduct rather than formation of the conjugate base (3). Two facts indicating that, at the base concentrations used, there is no substantial conversion of the parent into the diadduct (4; R = Me) are the observ-



Visible spectra of HNBB (2×10^{-5} M) and sodium ethoxide in ethanol. A, [NaOEt] 2×10^{-3} M after 2 min; B, same as A after 30 min (indicates irreversible reaction of substrate); C, [NaOEt] 4×10^{-3} M after 2 min

† $11 = 10^{-8}$ m².

ation of only one rate process and the value of the extinction coefficient which is too low for a diadduct (*cf.* ethoxide addition). It should be noted that the presence of dimethyl sulphoxide, used in the n.m.r. work, greatly increases the basicity of the medium ⁵ enabling formation of the diadduct (4; R = Me) to occur.

The n.m.r. work also indicates that in dimethyl sulphoxide addition at the 3-position to give (1; R = Me) precedes addition at the 1-position. Our failure to observe addition at the 3-position in methanol can be attributed to the low equilibrium constant expected for formation of this adduct. For comparison ⁶ the value of the equilibrium constant for methoxide attack at the 3-position of 2,4,6-trinitrotoluene in methanol is 0.07 l mol⁻¹.

TABLE 2

Equilibrium data for reaction of 2,2',4,4',6,6'-hexanitrobiphenyl ^a with sodium ethoxide in ethanol at 25 °C

	[NaOEt] ^b /M	OD (500 nm) observed	OD (500 nm) ^c calculated
1	0.001 01	0.192	0.190
2	0.002 02	0.245	0.253
3	0.004 04	0.297	0.311
4	0.007 06	0.357	0.356
5	0.0099	0.388	0.384
6	0.0199	0.428	0.445
7	0.0398	0.509	0.509
8	0.0597	0.538	0.544
9	0.0796	0.560	0.566
10	0.099	0.582	0.581
11	0.149	0.607	0.604
12	0.198	0.623	0.617

^a Concentration is 2.0×10^{-5} M. ^b In items 1—10 the solutions were made up to constant ionic strength, I 0.1M, with sodium perchlorate. ^c Calculated from equations (3)—(5) with values of K_1 1 200 l mol⁻¹, K_2 30 l mol⁻¹, $\epsilon(2; R = Et)$ 1.67×10^4 , $\epsilon(4; R = Et)$ 3.33×10^4 l mol⁻¹ cm⁻¹.

Reaction with Sodium Ethoxide in Ethanol.—Ethoxide in ethanol is a more basic medium than methoxide in methanol and here there is evidence that the formation of (2; R = Et) is preceded by the formation of (1; R = Et), and for the presence at equilibrium of the diadduct (4; R = Et).

Visible spectra were recorded for solutions containing 2×10^{-5} M-parent and 0.001—0.2M-sodium ethoxide. The spectra recorded after two minutes showed the double absorption maxima characteristic of σ -adduct formation.⁵ In the most dilute base concentration used the maxima were at 432 and 500 nm; in more concentrated base solutions the higher energy band shifted to 438 nm. Acidification of the solutions at this stage resulted in the regeneration of the parent. With time the bands due to σ -adducts were replaced by a band at 380 nm with broad shoulder at longer wavelength; acidification failed to regenerate the parent indicating that irreversible reaction had occurred.

Values of optical density after completion of the reaction giving σ -adducts but before decomposition had occurred are in Table 2. A Benesi-Hildebrand plot ⁷ of the reciprocal of optical density versus the reciprocal of base concentration was curved indicating that the reaction is more complicated than simple 1:1 adduct

formation. However a short extrapolation of the plot gave a value of 0.666 at 500 nm for complete conversion. From this we are able to calculate the values for the extinction coefficients for the species formed at the higher base concentrations. The values ϵ 6.0×10^4 (438 nm) and 3.33×10^4 l mol⁻¹ cm⁻¹ (500 nm) are approximately double those normally found for adducts of 1 : 1 stoichiometry.⁸ This strongly suggests that in the more concentrated base solutions used a diadduct is formed by ethoxide attack on the two benzene rings and in view of the n.m.r. evidence the most likely structure is (4; R = Et). Since the benzene rings are separated by two methylene groups it would be expected that the absorption would be twice that of a 1 : 1 adduct. Our data can be accommodated by the presence of two equilibria involving attack of ethoxide on one [equation (3)] or two rings [equation (4)]. Initially we obtained an approximate value for K_1 by assuming that in items 1—3 of

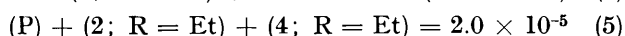
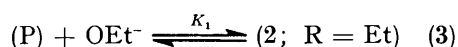
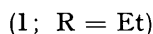


Table 2 there would be little of the diadduct present, and an approximate value for K_2 by assuming that in items 8—12 little parent would remain. By iteration we obtained values for K_1 of 1200 ± 200 l mol⁻¹ and K_2 of 30 ± 10 l mol⁻¹ which gave a good fit of calculated with observed optical densities. The considerably lower value for K_2 indicates that even though the 2,4,6-trinitrobenzene rings are separated by two methylene groups attack of alkoxide on one ring to give a σ -adduct inhibits attack on the second ring.

Examination by stopped flow spectrophotometry of solutions containing low (<0.01M) concentrations of base indicates the presence of two processes attributable to 1 : 1 interactions. The faster process which is of relatively low intensity gives rise to a species with maxima at 430 and 490 nm which is likely to be the



$$k_{\text{fast}} = k_3[\text{OEt}^-] + k_{-3} \quad (7)$$

$$k_{\text{slow}} = k_{-1} + k_1[\text{OEt}^-]/(1 + K_3[\text{OEt}^-]) \quad (8)$$

adduct (1; R = Et). The slower process giving an increase in intensity represents formation of the adduct (2; R = Et). Since the base concentration is in large excess over the parent concentration and the rates of the two processes are well separated it is readily shown by standard methods that equations (7) and (8) will apply. A linear plot of k_{fast} versus base concentration gave values for k_3 4000 l mol⁻¹ s⁻¹ and k_{-3} 32 s⁻¹. Combination of these values gives a value for K_3 of 125 l mol⁻¹ in good

agreement with that obtained from the optical densities at the completion of the fast process. The values of the slower rate process are accommodated by equation (8) with the values k_{-1} 0.070 s⁻¹, k_1 84 l mol⁻¹ s⁻¹, and K_3 125 l mol⁻¹.

TABLE 3

Kinetic data for 1 : 1 interaction of 2,2',4,4',6,6'-hexanitrobenzyl (1×10^{-5} M) with sodium ethoxide in ethanol at 25 °C

[NaOEt]/ M	$k_{\text{fast}}/$ s ⁻¹	OD (430 nm) ^a	K_3 ^b / l mol ⁻¹	$k_{\text{slow}}/$ s ⁻¹	k_{slow}^c (calc)
0.0010	36.5	0.0039	110	0.14	0.14
0.0015				0.18	0.18
0.0020	41	0.0092	150	0.21	0.20
0.0025				0.23	0.23
0.0040	48	0.0137	130	0.30	0.30
0.0060	52	0.0164	115	0.33	0.36
0.0084	66	0.0209	130		
0.0100	72	0.0218	120		

^a After completion of the fast process. 2 mm path length cell. A Benesi-Hildebrand plot gives a value of 0.040 for complete conversion. ^b Calculated from OD (430)/[0.040 - OD (430)][NaOEt]. ^c Calculated from equation (8) with k_{-1} 0.07 s⁻¹, k_1 84 l mol⁻¹ s⁻¹, and K_3 125 l mol⁻¹.

Comparison with Related Compounds.—Rate and equilibrium constants for 1 : 1 interaction are summarised in Table 4 where they are compared with data for 2,4,6-trinitrobenzyl chloride (TNBCl), 2,4,6-trinitrotoluene (TNT), and 1,3,5-trinitrobenzene (TNB). The data for 2,2',4,4',6,6'-hexanitrobenzyl (HNBB) have not been statistically adjusted.

The value of K_1 for ethoxide attack at the 1-position of HNBB is *ca.* 10 times higher than the value of K_3 for attack at the 3-position. Similarly TNBCl shows a thermodynamic preference for attack at the 1-position.⁴ This contrasts with the behaviour of TNT where σ -adducts are only observed from attack at the 3-position.^{6,9} One factor favouring alkoxide addition at the 1-position of HNBB or TNBCl, relative to TNT, is the inductive electron withdrawal of the 2,4,6-trinitrobenzyl or chlorine substituents. However steric factors are likely to be of importance. Thus the greater the size of the group at the 1-position the greater the possibility of relief of steric strain as the group is bent from the ring-plane in the 1-alkoxy-adduct.

Kinetically, attack at the unsubstituted ring positions is favoured over attack at the substituted positions. In particular the values for the rate coefficients for the reverse reactions appear to be characteristic of the position of addition. Thus, values of k_{-1} are at least 100 times lower than values of k_{-3} .

The values of K_3 for attack at unsubstituted positions are lowered by the presence of a bulky substituent at the 1-position. Thus for ethoxide additions the values decrease from TNB to TNBCl to HNBB. Nitro-groups will display their maximum electron-withdrawing ability when they are coplanar with the benzene ring and the presence of bulky substituents which cause their rotation from the ring-plane will be expected to cause a destabilising effect on addition at unsubstituted ring-positions.

A major reaction of both TNT and TNBCl with alk-

TABLE 4

Comparison of rate and equilibrium data for HNBB with those for related compounds

	$k_3/l \text{ mol}^{-1} \text{ s}^{-1}$	k_{-3}/s^{-1}	$K_3/l \text{ mol}^{-1}$	$k_1/l \text{ mol}^{-1} \text{ s}^{-1}$	k_{-1}/s^{-1}	$K_1/l \text{ mol}^{-1}$
HNBB-methoxide				23	1.15	20
TNCl-methoxide ^a			<20	770	2.2	350
TNT-methoxide ^b	280	3 000	0.07			
TNB-methoxide ^c	7 300	330	20			
HNBB-ethoxide	4 000	32	125	84	0.07	1 200
TNCl-ethoxide ^a	10 000	14	700	7 000	<1	>10 000
TNB-ethoxide ^c	40 000	20	2 000			

^a Ref. 4. ^b Ref. 6. ^c C. F. Bernasconi, *J. Am. Chem. Soc.*, 1970, **92**, 4682 (refers to addition at an unsubstituted position).

oxide ions is formation of the conjugate base by transfer of a side-chain proton.⁴ With both these substrates proton-transfer is a much slower process than base addition. Our data for HNBB do not provide any evidence for formation of the conjugate base (3), the ¹H n.m.r. and visible spectra being in accord with σ -adduct formation. We think it unlikely that the previously reported¹⁰ assignment of bands at 460 and 500 nm to the carbanion (3) is correct. We do however have evidence¹¹ for the presence in dimethyl sulphoxide containing the tertiary base 1,4-diazabicyclo[2.2.2]octane of a blue species with maximum at 650 nm which may be the anion (3) or some species derived from it.

The failure to observe (3) in solutions of base in alcohol is probably due to the slowness of its formation rather than its thermodynamic instability. We have shown that irreversible reaction of HNBB occurs fairly rapidly so that decomposition may occur before there is appreciable formation of (3).

EXPERIMENTAL

HNBB, m.p. 218–220 °C (lit.³ 218–220°), was provided by the Ministry of Defence. Solutions of sodium alkoxides were prepared by solution of clean pieces of sodium in AnalaR alcohol and were titrated against standard acid.

¹H N.m.r. measurements were made with a Varian EM 360L instrument using tetramethylsilane as internal reference. Visible spectral measurements were made with

Unicam SP 500 or 8000 instruments, or a Canterbury stopped-flow spectrophotometer. All kinetic measurements were made at 25 °C with base in large excess over substrate concentration.

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