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CINE SUBSTITUTION IN THE NAPHTHALENE SERIES. A KINETIC STUDY OF THE REACTION OF 2,3-DINITRONAPHTHALENE WITH PIPERIDINE IN BENZENE

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Although it has long been known that 2,3-dinitronaphthalene (1) reacts with nucleophiles to yield, as main or sole products, the corresponding 3-nitro-1-naphthyl derivatives,[1] to our knowledge no attempts have been made to interpret the mechanism of this reaction, which is indeed an interesting and rare[2] example of substitution reaction with rearrangement involving an aromatic nitro-group (*cine* substitution). As part of our program in this field, we report here a kinetic study of the reaction of (1) with piperidine (Pip) in benzene, which affords 1-piperidino-3-nitronaphthalene (2) in quantitative yield. Rate data are listed in the Table. Inspection of the Table reveals that the reaction is first-order with respect to (1), while the second-order rate coefficient k_2=rate/$[(1)][\mathrm{Pip}]$ rises steeply whith increasing $[\mathrm{Pip}]$ (in the range 0.2-1 M). Even the third-order rate coefficient k_3= rate/ $[(1)][\mathrm{Pip}]^2$ increases to some extent. However, the plot of k_3 *vs.* $[\mathrm{Pip}]$ is linear, according to the rate law: $k_3 = k' + k''[\mathrm{Pip}]$, where $k' = 4.6 \times 10^{-4}\ \mathrm{M}^{-2}\mathrm{sec.}^{-1}$ and $k'' = 1.2 \times 10^{-3}\ \mathrm{M}^{-3}\mathrm{sec.}^{-1}$ are third- and fourth-order coefficients respectively. On the basis of the magnitude of the ratio $k''/k' = 2.6\ \mathrm{M}^{-1}$ it is likely that the reaction of (1) with piperidine is an overall third-order process, first-order with respect to (1) and second-order with respect to piperidine. Thus, the moderate rise of k_3 with increasing $[\mathrm{Pip}]$ represents, in our opinion, a further example of mild acceleration which has been encountered in numerous other reactions and which does not seem to constitute evidence for base catalysis.[3] Furthermore, substitution of $[1\text{-}^2\mathrm{H}]$ piperidine for piperidine gives rise to a measurable isotope effect of *ca.* 2.5 (at $[\mathrm{Pip}]$ = 0.2 M), whilst both (1) and its 1,4-dideuteriated analogue react with piperidine at almost the same rate. Finally, n.m.r. analysis of the product of the reaction of (1) with $[1\text{-}^2\mathrm{H}]$ piperidine showed that incorporation of deuterium occurred only at the

TABLE

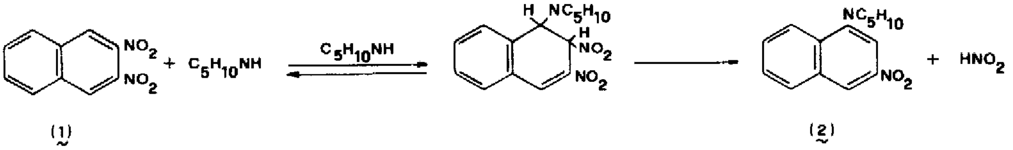
Rate coefficients for the reaction of 2,3-dinitro- or 1,4-dideuterio-2,3-dinitronaphthalene with piperidine or $[1\text{-}^{2}\text{H}]$piperidine in benzene at 50°.[a]

$[\text{Pip}]/\underline{\underline{M}}$	0.2	0.4	0.6	0.8	1.0	0.2[b]	0.2[c]	0.2[d]
$10^{4}k_{2}/\underline{\underline{M}}^{-1}\text{sec}^{-1}$	1.35	3.86	7.15	11.3	16.6	0.55	1.36	1.53
$10^{4}k_{3}/\underline{\underline{M}}^{-2}\text{sec}^{-1}$	6.75	9.65	11.9	14.1	16.6	2.75	6.80	7.65

[a] $[(1)] = 2.5 \times 10^{-3}$ M, unless otherwise stated. [b] Average of two runs carried out with $[1\text{-}^{2}\text{H}]$ piperidine *ca.* 83% deuteriated (i.r. analysis). [c] $[(1)] = 1.5 \times 10^{-3}$ M. [d] [1,4-dideuterio-2,3-dinitronaphthalene] $= 1.5 \times 10^{-3}$ M (*ca.* 85% deuteriated, by n.m.r. analysis).

position 2 of the naphthalene moiety.

Both an addition-elimination anomalous-type (AE_a) and an elimination-addition (EA) mechanism can account for the formation of (2). The type of nucleophile and of substrate and the second-order with respect to piperidine are consistent only



with an AE_a pathway, which is supported also by the lack of a measurable isotope effect in the reaction of the deuteriated (1) with piperidine and by the observed one in the reaction of (1) with $[1\text{-}^{2}\text{H}]$ piperidine. Furthermore, these last facts seem to suggest that the addition rather the elimination step is rate determining. It is likely that the second amine molecule operates the proton transference in the rate determining addition step.

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