Kinetics of the Formation of Dibenzotetraazapentalenes

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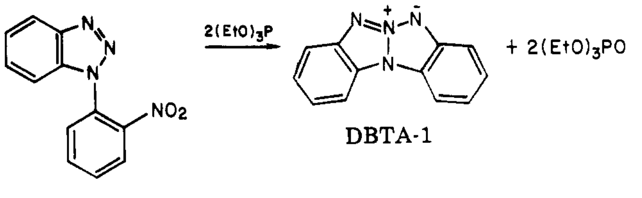
The kinetics for the formation of dibenzo-1,3a,6,6a-tetraazapentalene and dibenzo-1,3a,4,6a-tetraazapentalene from 1-(*o*-nitrophenyl)-1*H*-benzotriazole and 2-(*o*-nitrophenyl)-2*H*-benzotriazole with triethyl phosphite have been investigated. The reaction rates over a temperature range of 140–170 °C were measured by UV spectrophotometry. The reactions were found to be second order overall, insensitive to the dielectric constants of the solvents, and characterized by a large negative entropy of activation. These findings are consistent with the rate-determining step involving the formation of a four-membered cyclic transition state.

Dibenzo-1,3a,4,6a-tetraazapentalene (DBTA-2) was first reported to have been synthesized by the thermal decomposition of *o,o′*-diazidoazobenzene,[2] and studies have also reported[3,4] its decomposition mechanism. Recently it was reported that DBTA-2 and its isomer, dibenzo-1,3a,6,6a-tetraazapentalene (DBTA-1), had been prepared by a new method in which 2-(*o*-nitrophenyl)-2*H*-benzotriazole (2-NPB) and 1-(*o*-nitrophenyl)-1*H*-benzotriazole (1-NPB), respectively, are reduced and cyclized with triethyl phosphite (TEP).[5] The reduction of nitro compounds with TEP is generally considered to proceed via two steps;[6,7] the first step is a reduction to nitroso compounds, and then nitrene participated in the second step. The propriety of the proposal that nitrene is the intermediate in the latter step has been supported by identifying products obtained from hydrogen abstraction and C–H bond insertion in the deoxygenative reaction of 2′-nitroso-2,4,6-trimethylbiphenyl with TEP.[8] It has been proposed that reactions proceeding via the nitrene intermediate in the intramolecular cyclization of the nitroso compounds and TEP, as in this case, in general proceed stepwise via a nonconcerted mechanism.[9,10] On the contrary, it has also been reported recently that similar deoxygenative reactions by means of TEP are sequenced by a concerted mechanism in which the nitrene does not participate.[11-13] In the concerted mechanism reactions no byproducts have been observed.

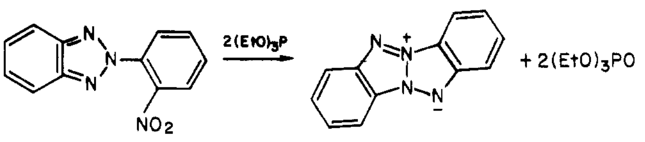
In this study, an attempt is made to elucidate in terms of chemical kinetics how the two isomers of tetraazapentalenes DBTA-1 and DBTA-2 are produced from 1- and 2-NPB with TEP (eq 1 and 2).



1-NPB

DBTA-1

(1)



2-NPB

DBTA-2

(2)

Results and Discussion

Since the UV absorbance of DBTA-1 is maximum at 363 nm, the rates of its formation were measured at this wavelength. In the case of reaction 2, absorption maxima appear at both 390 and 410 nm, but as the absorbance increment is larger at 410 nm, rates were measured at this wavelength. Second-order rate constants for varying temperatures and solvents obtained by this method are summarized in Table I. Activation parameters derived from the rate constants at 150.0 °C are tabulated in Table II, and the second-order plots are presented in Figure 1.

The results indicate that these are standard second-order reactions, and it can be seen from Table I that the rates of reaction for 1-NPB with TEP are always 3–4 times faster than those for 2-NPB regardless of reaction temperature or medium. Though this difference seems to be caused by a steric effect, it is not large enough to justify speculation on a different mechanism for the reaction. In addition, one is struck by the extreme similarity between the activation parameters of the isomeric DBTA-1 and -2 pairs. The most fundamental kinetic assumption that can be drawn from the fact that the reactions under investigation have such highly similar activation parameters is that the reaction mechanisms are almost certainly the same. Also noteworthy are the large negative values for the activation entropies under all the conditions used, below −38 eu in both reactions, and yet the difference between the activation entropies for the isomeric DBTA-1 and -2 pairs is only 2.0 eu. These findings imply that the rate-determining step must be highly restricted in freedom, and on the basis of many examples it is reasonable to assume that the transition state is most likely a charged transition state[14] or a cyclic form.[15,16] If the two reactions

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Table I. Solvent Effect on the Reaction Rates in the Formation of DBTA-1 and -2

	xylene	chlorobenzene	*o*-dichlorobenzene	HMPA[a]
ϵ^b	2.27-2.57	5.60	9.93	30.0
	$10^4 k_2$,[d] M^{-1} s^{-1}			
temp,[c] °C	xylene	chlorobenzene	*o*-dichlorobenzene	HMPA
	1-NPB (1.00×10^{-2} M) + TEP (4.00×10^{-2} M)			
140.0	4.43[e] ± 0.08	4.08 ± 0.07	4.51 ± 0.06	5.67 ± 0.08
150.0	7.87 ± 0.07	7.07 ± 0.09	7.92 ± 0.10	10.2 ± 0.9
160.0	12.9 ± 0.9	12.1 ± 0.8	13.3 ± 1.1	17.4 ± 0.8
170.0	21.7 ± 0.8	20.4 ± 0.6	22.1 ± 0.6	29.4 ± 0.9
	2-NPB (1.00×10^{-2} M) + TEP (4.00×10^{-2} M)			
140.0	1.19[e] ± 0.07	1.35 ± 0.10	1.55 ± 0.08	1.49 ± 0.10
150.0	2.08 ± 0.07	2.35 ± 0.09	2.75 ± 0.04	2.71 ± 0.12
160.0	3.55 ± 0.09	4.02 ± 0.05	4.51 ± 0.10	4.65 ± 0.09
170.0	5.88 ± 0.08	6.64 ± 0.09	7.64 ± 0.07	7.74 ± 0.08

[a] Hexamethylphosphoramide. [b] Dielectric constant. [c] Temperatures were maintained within ±0.2 °C. [d] Rate constants were obtained by least-squares methods with standard errors in individual measurements and are uncorrected for solvent expansion from room temperature. [e] The rate constants were, within experimental error, unchanged in the presence of 2.00×10^{-2} M cyclohexene for DBTA-1 and were reduced less than 10% for DBTA-2 at all temperatures used in this study.

Table II. Activation Parameters for the Formation of DBTA-1 and -2 in Various Solvents at 150.0 °C

	1-NPB (1.00×10^{-2} M) + TEP (4.00×10^{-2} M)		2-NPB (1.00×10^{-2} M) + TEP (4.00×10^{-2} M)	
solvent	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
xylene	18.4 ± 0.4[a]	−38.2 ± 1.0	18.5 ± 0.1	−40.5 ± 0.3
chlorobenzene	18.5 ± 0.5	−38.1 ± 1.1	18.5 ± 0.3	−40.3 ± 0.8
o-dichlorobenzene	18.4 ± 0.2	−38.1 ± 0.5	18.5 ± 0.4	−40.0 ± 1.0
HMPA	18.5 ± 0.5	−37.4 ± 1.2	18.5 ± 0.4	−39.9 ± 0.9

[a] The errors given were estimated from the extreme slopes of a $\ln k_2/T$ vs. $1/T$ plot.

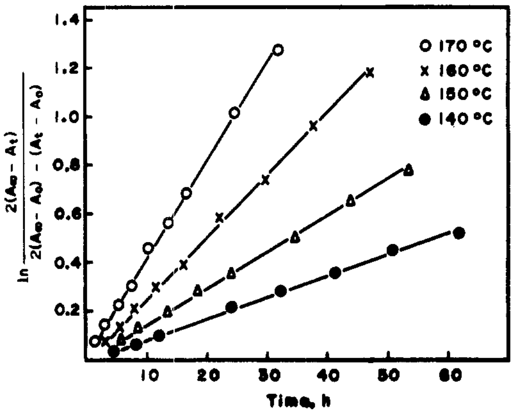

Figure 1. Second-order plots for the formation of DBTA-2 from 2-NPB in xylene; [2-NPB] = 1.00×10^{-2} M, and [TEP] = 4.00×10^{-2} M.

under examination proceed through a charged transition state, then it is strongly to be expected that the reaction rates would show appreciable sensitivity to the different dielectric constants of the solvent. However, the rate constants for each temperature under examination do not differ significantly in spite of the use of solvents which differ appreciably in their dielectric constants, and it is not likely that the transition state involves a charge separation. The large negative activation entropy of the reaction could suggest the existence of a cyclic transition state. The formation of the cyclic form would be consistent with the dual reactivity of the triethyl phosphite.[17] There are only two fundamentally different ways by which the reaction between NPB and TEP can take place. In the first, a phosphorus atom in TEP attacks a nitrogen atom of the NPB nitro group, and in the second the phosphorus atom attacks two oxygen atoms of the nitro group. It is clear that the former step is not applicable here on the basis of the fact that the final products, isomers of DBTA, are obtained by the deoxygenization of TEP. Thus, the most plausible structure for the transition state in these reactions is a four-membered cyclic form, and this explains the large negative entropy values and the solvent independence of the rate constants. This four-membered cyclic transition state will lead to intermediate **2**. It is not possible to prove directly that intermediate **2** exists, since it could not be isolated. There is, though, an alternative that can be considered regarding the cyclic transition state which is more favorable kinetically, and that is the possibility of a three-membered ring as the transition state.[18] In that case a small solvent effect would be observed if formation of the three-membered ring were rate determining. However, formation of the three-membered ring would be less favorable sterically compared to that of the four-membered ring. Also, once such a three-membered ring was formed, the resulting form would still have to undergo charge separation on the nitrogen and oxygen atoms which is unlikely in view of the small solvent effect. Therefore, the plausibility of the three-membered cyclic form as a transition state is considered unlikely. Next, it can readily be assumed that the transition from **2** to **3** is faster than the deoxygenation of NPB with TEP due to the instability of the four-membered cyclic intermediate **2**. And it also is apparent that the transition from **3** to the final product cannot be the rate-determining step on the basis of previous observations that the deoxygenation step of a nitroso compound is always faster than that of NPB with TEP.[7,8b,19] Thus, the rate-determining step is most

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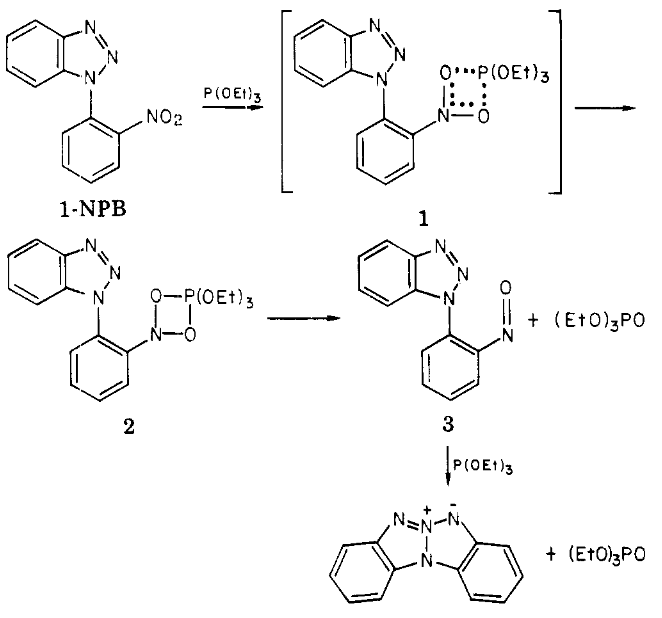
Scheme I



likely to be the formation of transition state 1, and this would be a concerted process. Finally, the possibility of a nitrene intermediary in the presence of cyclohexene has been examined by TLC analysis. However, no side products have been detected. Also, the reaction rates were not at all dependent on the presence of the trapping agent, as noted in Table I. Therefore, we believe that no nitrene was involved in the formation of DBTA from NPB with TEP. Thus, the mechanism proposed for this reaction is as shown in Scheme I.

Experimental Section

Materials. All solvents employed for kinetic measurements were purified by methods given in the literature.[20,21] Xylene (Riedel-De Haën Ag. Seele-Hannover, reagent grade) was dried over calcium chloride and distilled (137–138 °C). Chlorobenzene (Wako Chemical Co., reagent grade) was distilled in the presence of calcium chloride (131–131.5 °C). *o*-Dichlorobenzene (Wako Chemical Co., reagent grade) was treated with calcium chloride and distilled (179–180 °C). Hexamethylphosphoramide (HMPA) and triethyl phosphite (TEP; both Aldrich Chemical Co.) were treated with sodium and distilled under vacuum [97–99 °C (6 mm) and 49–50 °C (10 mm), respectively]. Cyclohexene,[22] 1-NPB,[3] 2-NPB,[3] DBTA-1,[5] and DBTA-2[5] were prepared by literature methods.

Kinetics. Rate constants were determined from measurements of increase in absorbance at 363 and 410 nm accompanying formation of DBTA-1 and DBTA-2, respectively. One-milliliter portions of a solution containing 1.00×10^{-2} M of NPB and 4.00×10^{-2} M of TEP in a specific solvent were pipetted into each of 12–15 Pyrex ampules. The solutions in the ampules were flushed with nitrogen gas and then sealed. All the ampules were placed simultaneously in an oil bath at room temperature, and the temperature of the oil bath was raised and maintained at a constant temperature (±0.2 °C) by a thermoregulator (Fisher Scientific Co., Model 280). Ampules were removed from the oil bath one at a time at appropriate time intervals and quenched in an ice–water mixture to stop further reaction. The first (zero time) ampule in a given run was removed from the oil bath when the temperature reached the specified temperature. From 10 to 12 ampules were used for each kinetic run. After all the quenched ampules had been allowed to reach thermal equilibrium (~1 h) at room temperature and were then opened, aliquots were diluted with the same solvent to 2.00×10^{-5} M with respect to the initially present NPB for the UV determinations. Absorbances were measured with a Shimadzu Model UV-200 double-beam spectrophotometer using a 1-cm quartz cell covered by a Teflon stopper. The second-order rate constants were obtained from the slopes of plots of $\ln\,[2(A_\infty - A_t)/2(A_\infty - A_0) - (A_t - A_0)]$ vs. time derived from $k_2 = [1/t(2a - b)] \ln\,[b(a - x)/a(b - 2x)]$ for our situation of $b = 4a$.[23a] The values of the activation parameters were obtained by using the Arrhenius plot at four different temperatures and the Eyring equation.[23b] Thin-layer chromatography was conducted on precoated silica gel IB-F sheets (J. T. Baker Chemical Co.) eluted with appropriate solvents.

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Registry No. DBTA-1, 2055-55-2; DBTA-2, 7120-73-2; 1-NPB, 2229-36-9; 2-NPB, 10560-89-1.

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