BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 1049—1054 (1966)

The Chemistry of Polyazanes. II. 1, 8-Di-*p*-tolyl-3, 6-diphenyl-1, 4, 7-octaaztriene

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(Received October 19, 1965)

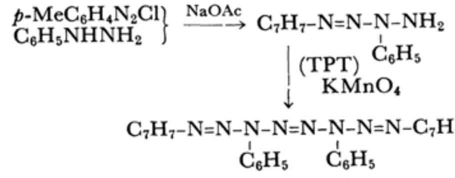
1, 8-Di-*p*-tolyl-3, 6-diphenyl-1, 4, 7-octaaztriene (DTDPO) was prepared by the potassium permanganate oxidation of 1-*p*-tolyl-3-phenyl-1-tetraazene (TPT), and the kinetics and the products of the decomposition of DTDPO were investigated. The experimental results can best be explained by assuming a mechanism in which DTDPO decomposes homolytically to yield a nitrogen molecule and two triazenyl radicals, which then combine to form 1, 3, 4, 6-tetraaryl-1, 5-hexaazdiene; the latter is very unstable and decomposes quickly to yield substituted azobenzenes and phenyl and *p*-tolyl radicals. The rather slow rate of decomposition of DTDPO was also discussed.

Except for carbon, very few elements are capable of forming compounds with chains of the same atoms linked linearly. Nitrogen is one of these few exceptions, and the polyazanes appear to be very interesting compounds. Our laboratories have been investigating the chemistry of various polyazanes; in this paper the chemistry of 1, 8-di-*p*-tolyl-3, 6-diphenyl-1, 4, 7-octaaztriene (DTDPO) will be described.

Wohl and Schiff1) reported on the synthesis of DTDPO by the oxidation of 1-*p*-tolyl-3-phenyl-1-tetraazene (TPT) with an aqueous potassium permanganate solution at 0°C. Although they reported that DTDPO was very unstable, no precise kinetic measurements were made, nor were the products of the decomposition studied. Therefore, this investigation was undertaken in order to determine the rates of decomposition, the activation parameters, and the products of the decomposition of DTDPO.

Results and Discussion

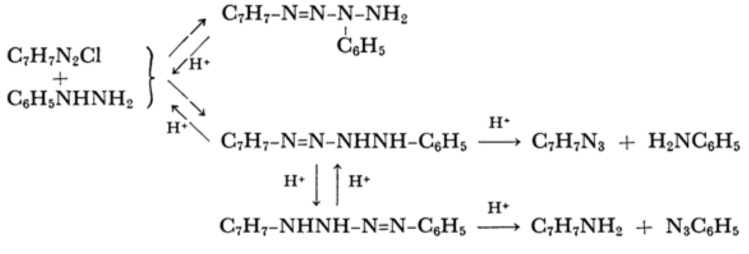
1, 8-Di-*p*-tolyl-3, 6-diphenyl-1, 4, 7-octaaztriene (DTDPO) was synthesized by the potassium permanganate oxidation of 1-*p*-tolyl-3-phenyl-1-tetraazene (TPT), which had been prepared from the coupling of *p*-toluenediazonium chloride with phenylhydrazine.



$$\left.\begin{matrix} p\text{-}MeC_6H_4N_2Cl \\ C_6H_5NHNH_2 \end{matrix}\right\} \xrightarrow{NaOAc} C_7H_7\text{-}N{=}N\text{-}\underset{C_6H_5}{N}\text{-}NH_2 \ \text{(TPT)} \xrightarrow{KMnO_4} C_7H_7\text{-}N{=}N\text{-}\underset{C_6H_5}{N}\text{-}N{=}N\text{-}\underset{C_6H_5}{N}\text{-}N{=}N\text{-}C_7H_7$$

(DTDPO)

In the reaction between *p*-toluenediazonium chloride and phenylhydrazine, the fact that the α-nitrogen, not the β-nitrogen, receives the electrophilic attack of the diazonium ion is worthy of attention. However, this fact should not be interpreted to mean that α-nitrogen is more basic than β-nitrogen. The analysis of the side products of this coupling reaction indicated the presence of aniline, *p*-toluidine, phenyl azide and *p*-tolyl azide, which are the decomposition products of 1, 4-diaryl-1-tetraazenes, the latter being formed by the attack of the diazonium ion on the β-nitrogen atom of the phenylhydrazine. Undoubtedly both the α- and β-nitrogens are attacked by electrophilic diazonium ions. The TPT formed is susceptible to the attack of a proton and goes back to the diazonium ion and phenylhydrazine when the medium is acid. 1, 4-Diaryl-1-tetraazenes are also susceptible to the attack of a proton, but for these compounds three reactions are possible; one is the back reaction, the



$$C_7H_7N_2Cl + C_6H_5NHNH_2 \underset{H^+}{\rightleftarrows} C_7H_7\text{-}N{=}N\text{-}\underset{C_6H_5}{N}\text{-}NH_2$$

$$C_7H_7N_2Cl + C_6H_5NHNH_2 \underset{H^+}{\rightleftarrows} C_7H_7\text{-}N{=}N\text{-}NHNH\text{-}C_6H_5 \xrightarrow{H^+} C_7H_7N_3 + H_2NC_6H_5$$

$$C_7H_7\text{-}N{=}N\text{-}NHNH\text{-}C_6H_5 \underset{H^+}{\overset{H^+}{\rightleftarrows}} C_7H_7\text{-}NHNH\text{-}N{=}N\text{-}C_6H_5 \xrightarrow{H^+} C_7H_7NH_2 + N_3C_6H_5$$

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* American Chemical Society-Petroleum Research Fund Scholar.

1) A. Wohl and H. Schiff, *Ber.*, **33**, 2741 (1900).

second is the isomerization by the transfer of the double bond on the nitrogen chain, and the third is decomposition to yield an azide and an amine. The only irreversible products formed from the various reactions described above are the azides and the amines. When the medium was sufficiently acid, the only products isolated were azides and amines, and no TPT was obtained. Even when a quantity of sodium acetate sufficient for the neutralization of the diazonium chloride was present, the formation of some azides and amines was unavoidable.

The crude TPT containing some moisture changed into azides and amines in three days, even at −17°C, whereas the recrystallized TPT remained unchanged for at least two weeks at −17°C. The pure TPT decomposed into only azides and amines when it was allowed to stand in the open air at room temperature for 50 hr. The crude TPT smoked and then exploded when allowed to stand at 30°C for ten minutes.

TPT is very soluble in benzene or toluene, and slightly soluble in methanol or ethanol. In all of these solvents, however, TPT gradually decomposed at room temperature, and the color of the solution changed into brownish red and then into dark brown. Apparently the backward reaction yielded some diazonium compounds which reacted further to produce the coloration. TPT is very soluble in methylene chloride and slightly soluble in carbon tetrachloride, but TPT decomposed very fast in these chlorinated hydrocarbons and the solutions became dark brown within five minutes.

DTDPO was prepared by oxidizing TPT with potassium permanganate below 0°C. The crude DTDPO could be purified by the recrystallization in ether at −73°C. The pure yellow crystals of DTDPO were rather stable at room temperature when no mechanical shock was applied. However, they violently exploded when scratched or rubbed. DTDPO crystals must be handled with extreme caution.

TABLE I. RATES OF DECOMPOSITION OF DTDPO IN CUMENE

Temp. °C	$10^5 k_1$ sec^{-1}	Half life min.
10.0	0.417	2760
20.0	1.90	605
30.0	9.35	123

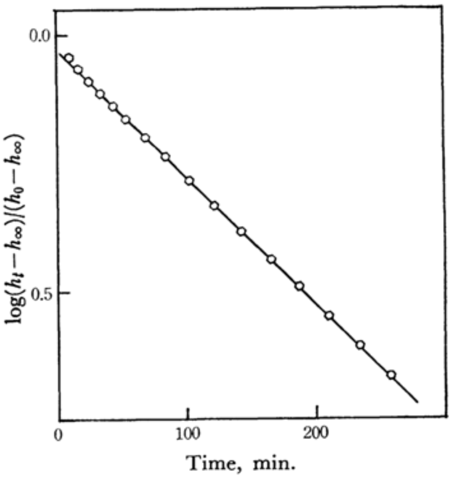


Fig. 1. Rate of decomposition of DTDPO in cumene at 30.0°C.
h_0, h_t and h_∞ are the difference of the mercury heights at $t=0$, $t=t$ and $t=\infty$, repectively.

The spontaneous decomposition of DTDPO was investigated by dissolving about one gram of DTDPO in about 40 ml. of cumene at lower temperatures and by warming up the solution to 10.0°C, 20.0°C and 30.0°C and keeping it there. The decomposition followed good first-order kinetics, as is seen in Fig. 1. The first-order rate constants at these three temperatures are shown in Table I, together with the half-lives. When $\ln(k/T)$ was plotted against $1/T$, a straight line was obtained, as is seen in Fig. 2. The values of the activation parameters obtained from the slope of Fig. 2 were $\Delta H^{\neq}=25.1$ kcal./mol. and $\Delta S^{\neq}=5.8$ e.u. Table II lists the products obtained

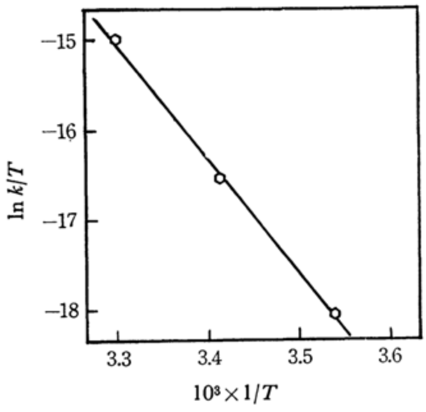


Fig. 2. $\ln k/T$ vs. $1/T$ for the decomposition of DTDPO.

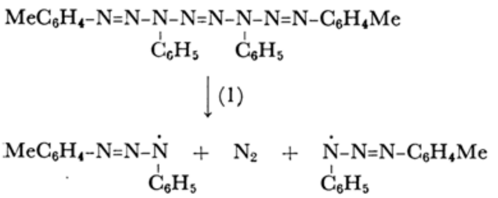
TABLE II. PRODUCTS OF DECOMPOSITION OF DTDPO IN CUMENE AT 30.0°C*

Product	mmol.	mol./mol. DTDPO
N_2	6.47	2.94
$C_6H_5N{=}NC_6H_5$	0.968	0.44
$MeC_6H_4N{=}NC_6H_5$	0.880	0.40
$MeC_6H_4N{=}NNHC_6H_5$	0.176	0.08
C_6H_6	1.45	0.66
C_6H_5Me	3.10	1.41
$(C_6H_5CMe_2)_2$	1.12	0.51

* 0.9878 g. of DTDPO (2.20 mmol.) was dissolved in 39.0 ml. of degassed cumene, and decomposed at 30.0°C for 24 hr.

from the decomposition of DTDPO at 30°C.

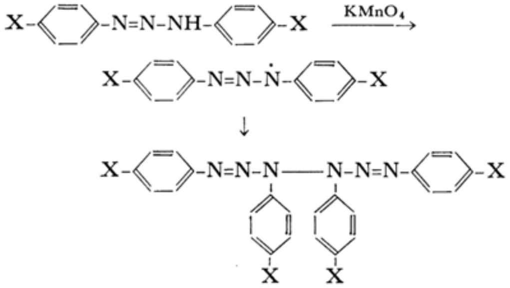
It is plausible that the initial step of the decomposition of DTDPO in inert solvents may be represented as follows:



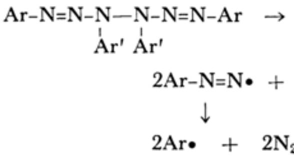
$$\mathrm{MeC_6H_4{-}N{=}N{-}\underset{C_6H_5}{N}{-}N{=}N{-}\underset{C_6H_5}{N}{-}N{=}N{-}C_6H_4Me} \xrightarrow{(1)} \mathrm{MeC_6H_4{-}N{=}N{-}\underset{C_6H_5}{\dot{N}}} + \mathrm{N_2} + \mathrm{\underset{C_6H_5}{\dot{N}}{-}N{=}N{-}C_6H_4Me}$$

The production of toluene, bezene, azobenzenes, and about three moles of nitrogen from a mole of DTDPO cannot be explained by the reaction 1. Obviously further consideration and refinement of the mechanism is necessary.

Theilacker and Fintelmann[2] oxidized 1, 3-diaryl-triazenes with potassium permanganate, thus obtaining unstable crystals of 1, 3, 4, 6-tetraaryl-1, 5-hexaazdienes from the triazenes substituted with electron-withdrawing groups on the arene rings.



When there are no substituents or when there are electron-releasing substituents on the arene rings, no hexaazdienes were obtained, only such decomposition products as azobenzenes. Even the hexaazdienes substituted with electron-withdrawing groups were rather unstable; they were found to decompose gradually, even in cold, yielding substituted azobenzenes.



$$\mathrm{Ar{-}N{=}N{-}\underset{Ar'}{N}{-}\underset{Ar'}{N}{-}N{=}N{-}Ar} \rightarrow 2\mathrm{Ar{-}N{=}N}\bullet + \mathrm{Ar'{-}N{=}N{-}Ar'}$$
$$\downarrow$$
$$2\mathrm{Ar}\bullet + 2\mathrm{N_2}$$

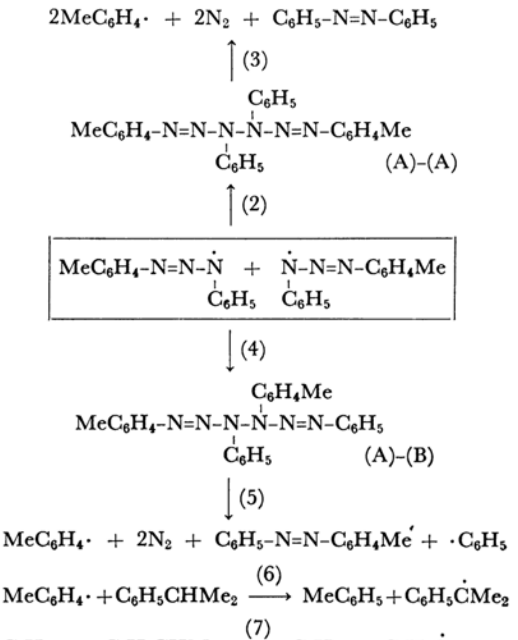
These facts appear to be quite relevant to the decomposition of DTDPO in cumene. It is likely that the diaryltriazenyl radicals formed by the reaction 1 combine to form 1, 3, 4, 6-tetraaryl-1, 5-hexaazdienes, which then rapidly decompose to yield substituted azobenzenes, toluene, benzene, and bicumyl. Since these arene rings are either nonsubstituted or substituted with electron-releasing groups, it is understandable that no hexaazdienes were found as the intermediates in the decomposition of DTDPO.

Table II shows that only a small amount of 1-*p*-tolyl-3-phenyltriazene was formed; one has therefore to assume that the majority of the triazenyl radicals combine with each other. This assumption is supported by the formation of almost three moles of nitrogen and considerable amounts of azobenzenes, benzene, toluene, and bicumyl. It is reasonable that the triazenyl radicals do not react with the solvent molecules and do not survive long enough to recombine with each other, since the triazenyl radical is more stable than the 1-methyl-1-phenylethyl radical, which is formed by hydrogen-abstraction from cumene by the triazenyl radical.

Since the triazenyl radical formed by the abstraction of a hydrogen atom from 1-*p*-tolyl-3-phenyltriazene is stabilized by the resonance:

$$\underset{\text{(A)}}{\mathrm{MeC_6H_4{-}N{=}N{-}\dot{N}{-}C_6H_5}} \leftrightarrow \underset{\text{(B)}}{\mathrm{MeC_6H_4{-}\dot{N}{-}N{=}N{-}C_6H_5}}$$

there are three possible combinations of these radicals: A and A, A and B, and B and B. Upon decomposition, A–A would yield azobenzene, the *p*-tolyl radical and nitrogen; A–B would yield 4-methylazobenzene, *p*-tolyl and phenyl radicals and nitrogen; B–B would yield 4, 4-dimethylazobenzene, the phenyl radical and nitrogen. Since no 4, 4-dimethylazobenzene was found in the decomposition products of DTDPO, the



$$2\mathrm{MeC_6H_4}\cdot + 2\mathrm{N_2} + \mathrm{C_6H_5{-}N{=}N{-}C_6H_5}$$
$$\Big\uparrow (3)$$
$$\mathrm{MeC_6H_4{-}N{=}N{-}\underset{C_6H_5}{N}{-}\overset{C_6H_5}{N}{-}N{=}N{-}C_6H_4Me} \qquad \text{(A)-(A)}$$
$$\Big\uparrow (2)$$
$$\boxed{\mathrm{MeC_6H_4{-}N{=}N{-}\underset{C_6H_5}{\dot{N}}} + \mathrm{\underset{C_6H_5}{\dot{N}}{-}N{=}N{-}C_6H_4Me}}$$
$$\Big\downarrow (4)$$
$$\mathrm{MeC_6H_4{-}N{=}N{-}\underset{C_6H_5}{N}{-}\overset{C_6H_4Me}{N}{-}N{=}N{-}C_6H_5} \qquad \text{(A)-(B)}$$
$$\Big\downarrow (5)$$
$$\mathrm{MeC_6H_4}\cdot + 2\mathrm{N_2} + \mathrm{C_6H_5{-}N{=}N{-}C_6H_4Me} + \cdot\mathrm{C_6H_5}$$

$$\mathrm{MeC_6H_4}\cdot + \mathrm{C_6H_5CHMe_2} \xrightarrow{(6)} \mathrm{MeC_6H_5} + \mathrm{C_6H_5\dot{C}Me_2}$$

$$\mathrm{C_6H_5}\cdot + \mathrm{C_6H_5CHMe_2} \xrightarrow{(7)} \mathrm{C_6H_6} + \mathrm{C_6H_5\dot{C}Me_2}$$

$$2\mathrm{C_6H_5\dot{C}Me_2} \xrightarrow{(8)} \mathrm{(C_6H_5CMe_2)_2}$$

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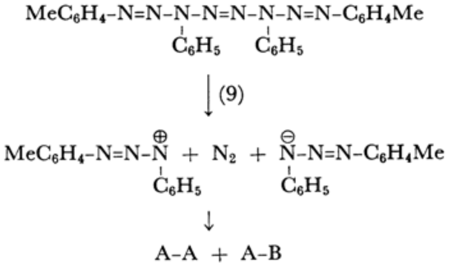
[2] W. Theilacker and E-C. Fintelmann, *Chem. Ber.*, **91**, 1597 (1958).

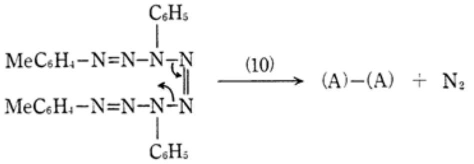
combination between B and B did not occur to any measurable extent. Both phenyl and *p*-tolyl radicals would abstract hydrogen atoms from cumene molecules, and the cumyl radicals thus produced would combine to form bicumyl molecules.

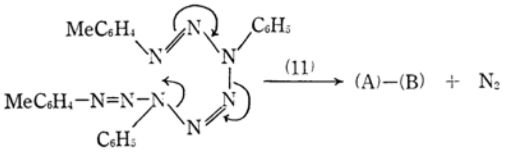
The reactions 1—8 are consistent with the experimental results and can account for all the products shown in Table II.

However, the formation of the 1, 3, 4, 6-tetraarylhexaazdienes, A-A and A-B, is possible by another route, namely, the heterolytic decomposition of DTDPO:

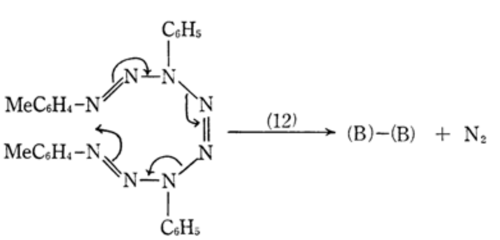


$$MeC_6H_4\text{-}N{=}N\text{-}\underset{C_6H_5}{N}\text{-}N{=}N\text{-}\underset{C_6H_5}{N}\text{-}N{=}N\text{-}C_6H_4Me \xrightarrow{(9)} MeC_6H_4\text{-}N{=}N\text{-}\underset{C_6H_5}{\overset{\oplus}{N}} + N_2 + \underset{C_6H_5}{\overset{\ominus}{N}}\text{-}N{=}N\text{-}C_6H_4Me \rightarrow A\text{-}A + A\text{-}B$$





Although B-B was not found in the decomposition products, the formation of B-B is also possible by a similar cyclic route:



The heterolytic decomposition of DTDPO and the subsequent decomposition of hexaazdienes (i. e., the reactions 9, 10, 11, 3, 5, 6, 7, and 8) can account for all the products shown in Table II.

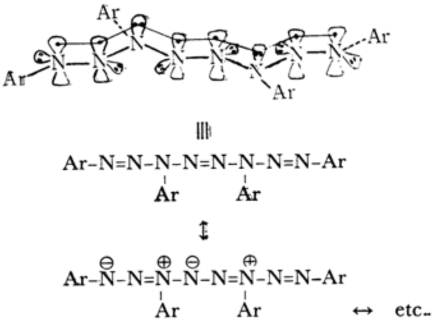
The choice between the homolytic mechanism and the heterolytic mechanism for the decomposition of DTDPO cannot be made easily. However, the homolytic mechanism (Reactions 1—8) seems more plausible than the heterolytic mechanism (Reactions 9, 10, 11, 3, 5, 6, 7 and 8), in view of the facts that: (a) the activation parameters ($\Delta H^{\neq}=25.1$ kcal./mol., $\Delta S^{\neq}=5.8$ e. u.) are consistent with a homolytic decomposition rather than a heterolytic decomposition, and (b) the symmetric azo compounds or peroxides rarely undergo heterolytic decomposition.

TABLE III. RATES OF DECOMPOSITION OF VARIOUS AZO COMPOUNDS

Azo compound	Solvent	Temp. °C	10^4k_1 sec^{-1}	Ref.
Me–N=N–Me	(Gas)	300	5.6	5
$Me_2(NC)C$–N=N–$C(CN)Me_2$	Xylene	80	1.53	6
Ph–N=N–$CHPh_2$	Decalin	54	1.01	7
Ph–N=N–CPh_3	Toluene	53	2.25	8
	Benzene	25	0.042	9
DTDPO	Cumene	20	0.190	
C_7H_7–N=N–N(C_7H_7)–N=N–C_7H_7	Cumene	25.8	12.9	4

In Table III, the rate of the decomposition of DTDPO is compared with the rates of the decomposition of several azohydrocarbons. The fact that DTDPO is more stable than 1, 3, 5-tri-*p*-tolyl-1, 4-pentaazdiene is rather surprising. This fact should be discussed further.

The lone-pair electrons of 3- and 6-nitrogen atoms of DTDPO are in resonance with the *p*-orbitals of azo linkages; hence, these orbitals



$$Ar\text{-}N{=}N\text{-}\underset{Ar}{N}\text{-}N{=}N\text{-}\underset{Ar}{N}\text{-}N{=}N\text{-}Ar$$

$$\updownarrow$$

$$Ar\text{-}\overset{\ominus}{N}\text{-}N{=}\underset{Ar}{\overset{\oplus}{N}}\text{-}\overset{\ominus}{N}\text{-}N{=}\underset{Ar}{\overset{\oplus}{N}}\text{-}N{=}N\text{-}Ar \quad \leftrightarrow \quad \text{etc.}$$

Fig. 3(a)

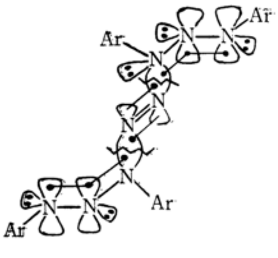


Fig. 3(b)

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[3] A. Wohl and H. Schiff, *Ber.*, **26**, 1587 (1893).

[4] H. Minato and M. Oku, This Bulletin, **38**, 1529 (1965).

[5] O. K. Rice and D. V. Sickman, *J. Chem. Phys.*, **4**, 239, 242, 608 (1936).

[6] C. G. Overberger, M. T. O'Shaughnessy and H. Shalit, *J. Am. Chem. Soc.*, **71**, 2661 (1949).

[7] S. G. Cohen and C. H. Wang, ibid., **77**, 3628 (1955).

[8] S. G. Cohen and C. H. Wang, ibib., **75**, 5504 (1953).

[9] M. G. Alder and J. E. Leffler, ibid., **76**, 1425 (1954).

are probably parallel with one another, as is shown in Fig. 3(a). When the molecule of DTDPO with the structure shown in Fig. 3(a) is to decompose, the $\mathrm{MeC_6H_4N{=}N{-}\dot{N}{-}C_6H_5}$ radical to be formed in the transition state does not have the resonance energy which is available to the molecules with the 3(b) structure. The rotation of the groups in 3(a) to obtain 3(b) is possible in solution. However, the molecule of DTDPO possesses four bulky arene rings on the chain of eight nitrogen atoms; it is very rare for the molecule of DTDPO with so much freedom to have the orientation represented in Fig. 3(b). Thus, the extremely small possibility of attaining a transition state stabilized with the resonance represented in Fig. 3(b) may be the reason for the rather slow rate of decomposition of DTDPO.

Experimental

Materials.—Tokyo Kasei Co. G. R. cumene was shaken with portions of concentrated sulfuric acid until the acid layer no longer became colored on long shaking. After washing with water, a sodium bicarbonate solution, and water again, the cumene was dried with calcium chloride and distilled from sodium through a 90-cm. column packed with glass helices. The center fraction, boiling at 152—153.2°C, was stored under nitrogen atmosphere and used.

All the other chemicals were those of the best grade commercially available, and were used without further purification.

The Synthesis of 1-*p*-Tolyl-3-phenyl-1-tetraazene (TPT).—The method of Wohl and Schiff[3] was modified a little. Into a mixture of 22 g. of *p*-toluidine (0.2 mol.) and 30 ml. of water, 52 ml. of concentrated hydrochloric acid (0.6 mol.) was added. The mixture was heated to dissolve its elements, and then the solution was cooled thoroughly by adding cracked ice to it and by placing it in an ice bath. The diazotization was carried out at 0°C by adding a solution of 14 g. of sodium nitrite (0.2 mol.) in 40 ml. of water the toluidine hydrochloride solution drop by drop.

Into a mixture of 22 g. of phenylhydrazine (0.2 mol.), 50 ml. of water, and 12 g. of acetic acid (0.2 mol.), a solution of 82 g. of sodium acetate (1 mol.) in 20 ml. of acetic acid and 120 ml. of water was added all at once; the mixture was then cooled to 0°C. Into this phenylhydrazine mixture the *p*-toluenediazonium chloride solution was stirred in portions at temperatures between 0 and 2°C. A light yellow substance was formed at once and floated on the surface of the water layer. It changed to a yellowish brown after one hour of stirring in an ice bath. The crude brown product was then collected by filtration; 22 g. (50%). The melting point of the crude product was 63—67°C, but when 22 g. of the crude product was recrystallized in ether at −73°C, 9.8 g. of fine yellow crystals was obtained, melting at 74.5°C with gas evolution (reported by Wohl and Schiff, 66—67°C).[1]

The Synthesis of 1,8-Di-*p*-tolyl-3,6-diphenyl-1,4,7-octaaztriene (DTDPO).—The method of Wohl and Schiff[1] was modified a little. After two grams of TPT had been dissolved in 25 ml. of ether cooled at 0°C, the solution was cooled to −12°C. Into this cold TPT solution, 50 ml. of a 1% potassium permanganate solution was added slowly over a 20-min. period A pale yellow substance gradually appeared and floated at the top of the upper ethereal layer, and the violet color of potassium permanganate changed to dark brown. The mixture was stirred for 30 min. at −4—1°C after the potassium permanganate solution had been added.

The two layers were then separated with a separatory funnel, and the pale yellow product, contaminated with some black manganese dioxide, was filtered from the ethereal layer. Fifteen milliliters of a 3% sulfurous acid solution cooled to 0°C was added to the residue in the funnel in order to wash away the black manganese dioxide. The crude DTDPO was then washed well with cold water. The yield of the crude DTDPO was 0.6 g.; m. p. 61.5—64°C (with an evolution of gas).

The slightly wet DTDPO (0.6 g.) was dissolved in 5 ml. of ether at room temperature, and the solution was cooled to −73°C. The ice formed was removed by decantation. After 10 min. at −73°C, light yellow needles were formed and collected by filtration. The yield was 0.3 g.; m. p. 65.5—66.0°C (reported by Wohl and Schiff[1], 64—67°C).

The crystals of DTDPO are extremely sensitive to mechanical shock. After the crystals had been dried by an aspirator for about four minutes at room temperature, and the rubber tubing had then been taken off, the stream of air suddenly flowing into the vessel was a shock sufficient to cause an explosion of DTDPO crystals. DTDPO also exploded when it was rubbed in a mortar, or when it was dropped into concentrated hydrochloric or sulfuric acid.

When crystals of DTDPO were dissolved in carbon tetrachloride, dichloromethane, ether or toluene at room temperature, they quickly decomposed, with an evolution of gas. However, the solid DTDPO was rather stable when there was no mechanical shock. The crystals of DTDPO did not decompose at all when kept at −17°C in darkness for at least three weeks; the melting point of crystals decreased by only 1—2°C when they were placed in the open air for two days. The fact that it is rather stable as a solid but unstable in a solution is reminiscent of the behavior of 1,3,5-tri-*p*-tolyl-1,4-pentaazdiene.[4]

Kinetic Procedure.—About 1 g. of DTDPO was placed in a glass vessel attached to an end of a U-shaped tube, and then about 40 ml. of cumene was

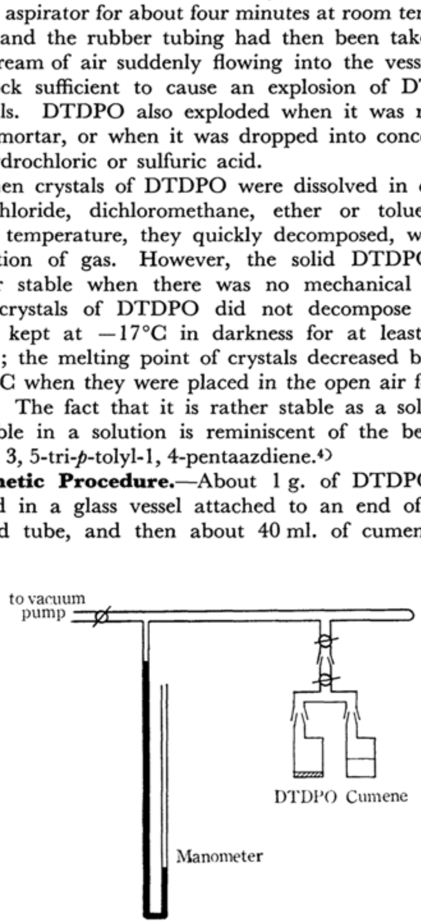

Fig. 4

placed in a glass vessel attached to the other end of the U-shaped tube, as is shown in Fig. 4. These two were degassed and then mixed at −78°C. Then this U-tube was attached to a vacuum system of a known volume with the mercury manometer. The U-tube was immersed in a small bath of a constant temperature by elevating the bath with a lab-jack. By turning a stopcock, the U-tube was opened to the evacuated system, and the increase in the pressure of the system was measured versus the time. After the U-tube had been warmed to the temperature of the bath, the plots of the increase in the pressure showed good first-order behavior. The infinity point was taken after about ten half-lives.

Procedure for Product Studies.—The DTDPO solution used for kinetic studies was analyzed for the products of decomposition. The amount of nitrogen was determined from the data on the pressure, the volume and the temperature of the system. The cumene solution was distilled to yield brownish solids and a distillate. When the distillate was investigated by a Shimadzu Gas Chromatograph GC-2B, the peaks corresponding to benzene and toluene were observed, in addition to the peak of cumene. The amounts of benzene and toluene were determined by using ethanol as the internal standard.

The infrared spectrum of the brownish residue showed the absorptions of bicumyl (2, 3-dimethyl-2, 3-diphenylbutane), azobenzene, 4-methylazobenzene, and 3-phenyl-1-*p*-tolyltriazene. The elution chromatography of these brownish solids on alumina yielded bicumyl as the first fraction, a mixture of azobenzene and 4-methylazobenzene as the second fraction, and 3-phenyl-1-*p*-tolyltriazene as the last fraction. The identity of bicumyl and 3-phenyl-1-*p*-tolyltriazene was established by comparing their melting points and infrared spectra with those of authentic samples. The amounts of azobenzene and 4-methylazobenzene were determined by comparing the infrared spectrum of the mixture with those of authentic samples, and finally by preparing a synthetic mixture of azobenzene and 4-methylazobenzene; the infrared spectrum of this synthetic mixture was identical with that of the mixture derived from the reaction products.

Grateful acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research.