The Chemistry of Polyazanes. I. The Decomposition of 1, 3, 5-Tri-*p*-tolyl-1, 4-pentazdiene

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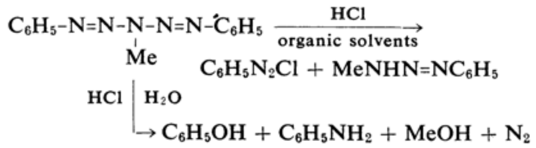
(Received February 19, 1965)

Although the organic compounds containing a chain of more than three nitrogen atoms appear to be very interesting, they have not been fully investigated. Our laboratories have, therefore, been investigating the chemistry of various polyazanes; in this paper the chemistry of 1, 3, 5-tri-*p*-tolyl-1, 4-pentazdiene (TTP) will be described.

Pechmann and Frobenius[1] studied the syntheses of TTP and other pentazdienes and found that these compounds underwent the following decomposition:



$$C_6H_5\text{-}N{=}N\text{-}\underset{\displaystyle Me}{\underset{|}{N}}\text{-}N{=}N\text{-}C_6H_5 \xrightarrow[\text{organic solvents}]{\text{HCl}} C_6H_5N_2Cl + MeNHN{=}NC_6H_5 \xrightarrow[\text{HCl}]{H_2O} C_6H_5OH + C_6H_5NH_2 + MeOH + N_2$$

Wicklatz[2] prepared TTP and other pentazdienes, and used these compounds as the initiators of the emulsion polymerization of butadiene and styrene at 0—50°C. Hall and Seed[3] used 1, 5-diaryl-3-alkyl-1, 4-pentazdienes as the initiators of the polymerization of ethylene at 120—150°C and of methyl methacrylate at 40°C. Rondestvedt and Davis[4] reported on the syntheses of 1, 5-diaryl-3-methyl-1, 4-pentazdienes as the by-products of the syntheses of triazenes. However, the spontaneous decomposition of 1, 3, 5-trisubstituted 1, 4-pentazdienes has never been investigated.

Results and Discussion

1, 3, 5-Tri-*p*-tolyl-1, 4-pentazdiene (TTP) was obtained as a yellow solid when two moles of *p*-toluenediazonium chloride and one mole of *p*-toluidine were coupled in the presence of sodium methoxide, according to the method of Pechmann and Frobenius.[1] TTP is sparingly soluble in diethyl ether, alcohols or ligroin. It dissolves in acetone, benzene or chloroform, with a rapid evolution of nitrogen, at room temperature. The recrystallization of TTP is possible when it is handled quickly in ether, benzene or acetone-water at 0°C.

The spontaneous decomposition of TTP was investigated by dissolving one gram of TTP in one hundred milliliters of cumene at lower temperatures and by keeping the solution at 0°C, 15.0°C or 25.8°C. The decomposition followed good first-order kinetics, as may be seen in Fig. 1. The first-order rate constants at those 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 may be seen in Fig. 2. The values of activation parameters obtained from the slope of Fig. 2 were $\Delta H^{\ne} = 22.6$ kcal./mol. and $\Delta S^{\ne} = 3.8$ e. u. Table II lists the products obtained from the decomposition of TTP at 25.8°C.

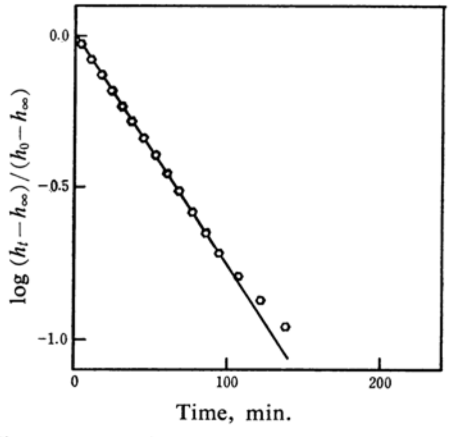


Fig. 1. Rate of decomposion of TTP in cumene at 15.0°.
h_0, h_t and h_∞ are the difference of the mercury heights at $t=0$, $t=t$ and $t=\infty$, respectively.

TABLE I. RATES OF DECOMPOSITION OF TTP IN CUMENE

Temp. °C	k_1 sec^{-1}	Half life min.
25.8	12.9×10^{-4}	8.95
15.0	2.93×10^{-4}	39.2
0.0	0.325×10^{-4}	354

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* American Chemical Society-Petroleum Research Fund Scholar.

[1] H. V. Pechmann and L. Frobenius, *Ber.*, **27**, 705 (1894).

[2] J. E. Wicklatz, U. S. Pat. 2530497 (1950); 2564632 (1951).

[3] W. Hall and L. Seed, Japanese Pat. 11791 (1960).

[4] C. S. Rondestvedt, Jr., and S. J. Davis, *J. Org. Chem.*, **22**, 200 (1957).

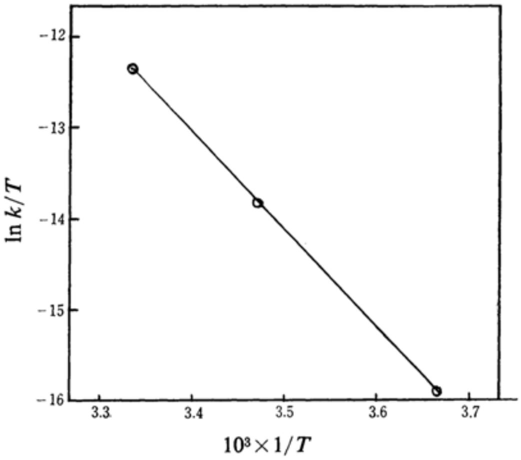


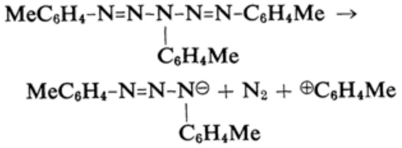
Fig. 2. ln k/T versus $1/T$ for the decomposition of TTP.

TABLE II. PRODUCTS OF DECOMPOSITION OF TTP IN CUMENE AT 25.8°*

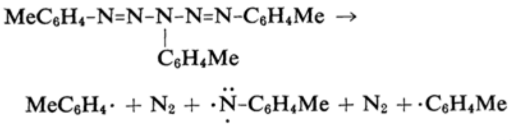
Product	mmoles	moles/mole TTP
N_2	2.52	0.871
$MeC_6H_4N{=}NNHC_6H_4Me$	2.90	0.994
MeC_6H_5	2.58	0.884
$(C_6H_5CMe_2)_2$	1.18	0.405

* 1.000 g. of TTP (2.91 mmol.) was dissolved in 100.0 ml. of cumene, and decomposed at 25.8°C for 20 hr. in the absence of air.

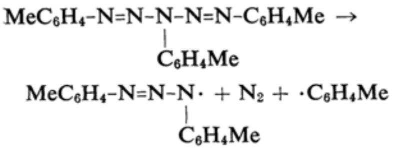
The three most plausible mechanisms of the decomposition of TTP in inert solvents are the following:



$$MeC_6H_4\text{-}N{=}N\text{-}\underset{\substack{|\\ C_6H_4Me}}{N}\text{-}N{=}N\text{-}C_6H_4Me \rightarrow MeC_6H_4\text{-}N{=}N\text{-}\underset{\substack{|\\ C_6H_4Me}}{N^{\ominus}} + N_2 + {}^{\oplus}C_6H_4Me \qquad (1)$$



$$MeC_6H_4\text{-}N{=}N\text{-}\underset{\substack{|\\ C_6H_4Me}}{N}\text{-}N{=}N\text{-}C_6H_4Me \rightarrow MeC_6H_4\cdot + N_2 + \cdot\overset{\cdot\cdot}{\underset{\cdot}{N}}\text{-}C_6H_4Me + N_2 + \cdot C_6H_4Me \qquad (2)$$

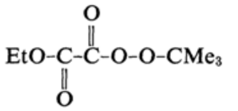


$$MeC_6H_4\text{-}N{=}N\text{-}\underset{\substack{|\\ C_6H_4Me}}{N}\text{-}N{=}N\text{-}C_6H_4Me \rightarrow MeC_6H_4\text{-}N{=}N\text{-}\underset{\substack{|\\ C_6H_4Me}}{N}\cdot + N_2 + \cdot C_6H_4Me \qquad (3)$$

Mechanism 1 cannot, however, account for the production of toluene and 2, 3-dimethyl-2, 3-diphenylbutane. Mechanism 2 can account for the production of these two hydrocarbons, but it cannot account for the production of 1, 3-di-*p*-tolyl-triazene. Only mechanism 3 is consistent with the experimental results. Thus the mode of the decomposition of TTP resembles that of azohydrocarbons, which decompose to yield a nitrogen molecule and two free radicals.

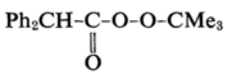
In Table III the rate of the decomposition of TTP is compared with the rates of the decomposition of several azohydrocarbons. The fact that TTP decomposes about 300 times as fast as 1′, 1′, 1′-triphenylbenzeneazomethane is rather surprising. The order of the increasing ease of decomposition in the series of azomethane, azobisisobutyronitrile, 1′, 1′-diphenylbenzeneazomethane and 1′, 1′, 1′-triphenylbenzeneazomethane may be ascribed to the production of free radicals with an increasing stability. However, it is difficult to suppose that the resonance energy of $MeC_6H_4\dot{N}\text{-}N{=}N\text{-}C_6H_4Me$ is greater than that of the triphenylmethyl radical. Therefore, some factors in addition to the resonance energy must be responsible for the rapid decomposition of TTP.

It has been found that peroxyoxalates decompose relatively fast among various peroxyesters.[10-15] The similarity of the rate of decomposition of ethyl *t*-butylperoxyoxalate to



$$EtO\text{-}\underset{\substack{\|\\ O}}{C}\text{-}\overset{\substack{O\\ \|}}{C}\text{-}O\text{-}O\text{-}CMe_3$$

Half life at 60°C, 35.6 min.



$$Ph_2CH\text{-}\underset{\substack{\|\\ O}}{C}\text{-}O\text{-}O\text{-}CMe_3$$

Half life at 60°C, 26 min.

that of *t*-butyl diphenylperoxyacetate suggests that the ethoxycarbonyl radical is about as stable as the diphenylmethyl radical. However, since the ethoxycarbonyl radical has no special structural characteristic which might account for this apparent stabilization, it is likely that the rate difference is due to the ease of the cleavage of the carbon-carbon bond of oxalates rather than to any special stabilization of the carbon radical formed. This reasoning may also be applicable to the rapid decomposition of TTP. Just as the decomposition of peroxyoxalates is aided by the repulsion

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

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

7) S. G. Cohen and C. H. Wang, *J. Am. Chem. Soc.*, **77**, 3628 (1955).

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

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

10) P. D. Bartlett and R. R. Hiatt, ibid., **80**, 1398 (1958).

11) P. D. Bartlett, E. P. Benzing and R. E. Pincock, ibid., **82**, 1756 (1960).

12) P. D. Bartlett and R. E. Pincock, ibid., **82**, 1769 (1960).

13) P. D. Bartlett and H. Sakurai, ibid., **84**, 3269 (1962).

14) P. D. Bartlett, B. A. Contarev and H. Sakurai, ibid., **84**, 3101 (1962).

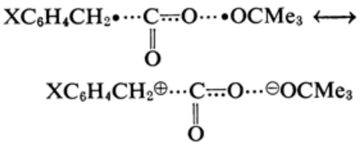
15) P. D. Bartlett and L. B. Gortler, ibid., **85**, 1864 (1963).

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	6)
$Me_2(NC)C-N=N-C(CN)Me_2$	Xylene	80	1.53	5)
$Ph-N=N-CHPh_2$	Decalin	54	1.01	7)
$Ph-N=N-CPh_3$	Toluene	53	2.25	8)
	Benzene	25	0.042	9)
$C_7H_7-N=N-N(C_7H_7)-N=N-C_7H_7$	Cumene	25.8	12.9	

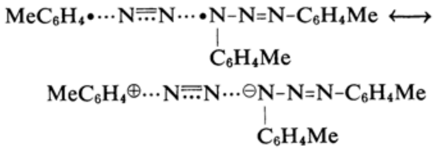
of the two central positively-polarized carbon atoms, the decomposition of TTP is aided by the repulsion of the electronegative nitrogen atoms, which weakens the bond between N_b and N_c in the structure $MeC_6H_4-N_a=N_b-N_c-(C_6H_4Me)-N_b=N_a-C_6H_4Me$.

In a number of cases, polar substituent effects have been discerned in the reactions of homolytic cleavage. For instance, Bartlett and Rüchardt[16] found that the thermal decomposition of substituted phenylperoxyacetates fits the Hammett equation when σ^+ is used rather than σ, and the observed ρ value was -1.04 at 100°C. The transition state has been pictured as a resonance hybrid of ionic and radical structures:



$$XC_6H_4CH_2\bullet\cdots\underset{\underset{O}{\|}}{C}\overset{\cdots}{=}O\cdots\bullet OCMe_3 \longleftrightarrow$$
$$XC_6H_4CH_2\oplus\cdots\underset{\underset{O}{\|}}{C}\overset{\cdots}{=}O\cdots\ominus OCMe_3$$

In a similar fashion, the transition state of the decomposition of TTP can be presented as a resonance hybrid of ionic and radical structures:



$$MeC_6H_4\bullet\cdots N\overset{\cdots}{\equiv}N\cdots\bullet \underset{\underset{C_6H_4Me}{|}}{N}-N=N-C_6H_4Me \longleftrightarrow$$
$$MeC_6H_4\oplus\cdots N\overset{\cdots}{\equiv}N\cdots\ominus \underset{\underset{C_6H_4Me}{|}}{N}-N=N-C_6H_4Me$$

The ionic form had a negative charge on the electronegative nitrogen atom, and this is a favorable form. The contribution of the ionic form to the transition state will reduce the activation energy required for the decomposition of TTP. Hence, this may be one of the factors responsible for the rapid decomposition of TTP.

One of the remarkable features of TTP is that it is very stable as a solid, whereas it is unstable in a solution. As has been described above, the half life of TTP is 9.0 min. at 25.8°C, but no apparent decomposition was observed for the solid TTP when it was allowed to stand at room temperature for several weeks. Such unusual behavior was never observed in other free radical initiators, such as peroxides and azohydrocarbons. The reason for the abnormal behavior of TTP is not clear, but the following speculation is attractive.

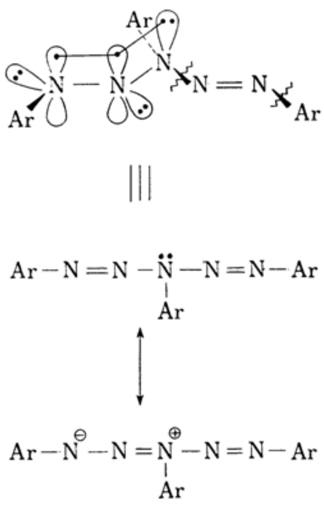


Fig. 3(a)

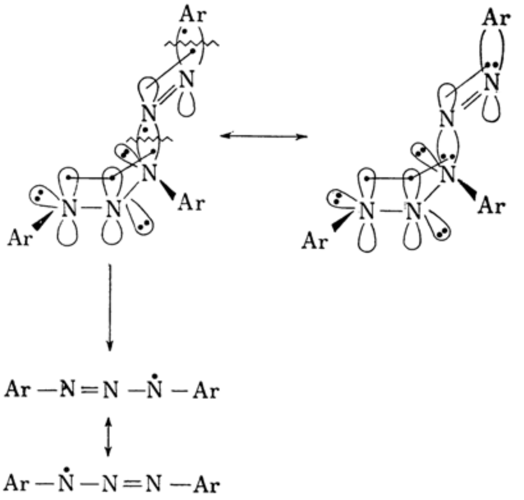


Fig. 3(b)

The lone pair electrons of the central nitrogen atom of TTP are in resonance with the *p*-orbitals of azo linkages, and hence these orbitals are parallel with one another, as is shown in Fig. 3(a). The structure of solid TTP is

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[16] P. D. Bartlett and C. Rüchardt, ibid., 82, 1756 (1960).

fixed as such. However, when the molecule of TTP with the structure shown in Fig. 3(a) is to decompose, the radical $\mathrm{MeC_6H_4N{=}\dot{N}NC_6H_4Me}$ to be formed at the transition state does not have the resonance energy which is available for the molecules with the structure 3(b). The rotation of the groups in 3(a) to obtain 3(b) is possible in solution, but it is not possible in solids. This might be the reason why TTP is very unstable in solutions, though it is very stable as a solid.

Wicklatz[2] reported that a mixture of 72 parts of butadiene and 28 parts of styrene slowly polymerized and that the conversion of 90.6% was attained in 11 hr. when the monomers were mixed with 180 parts of water, 5 parts of soap flakes and 3.43 parts of TTP at 50°C. The slow rate of the decomposition of TTP in this system is surprising compared with the half life of 9.0 min. in cumene at 25.8°C. Although TTP dissolves in styrene, it does not dissolve in ligroin, diethyl ether or alcohols, and hence it would probably not dissolve in butadiene. The solubility of TTP in the mixture of butadiene and styrene may be very small, especially when they are scattered as oil droplets covered with soap molecules in the aqueous phase. Therefore, the slow prolonged polymerization may be ascribed to the fact that TTP is sparingly soluble in this emulsified system. As soon as molecules of TTP dissolve at 50°C, they will quickly decompose to yield free radicals, which in turn initiate the polymerization of butadiene and styrene.

Experimental

Materials.—Tokyo Kasei Co. G. R. cumene was shaken wih portions of concentrated sulfuric acid until the acid layer no longer became colored upon long shaking. After it had been washed 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—152.3°C was stored under a nitrogen atmosphere and used.

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

The Synthesis of 1, 3, 5-Tri-*p*-tolyl-1, 4-pentazdiene (TTP). — The method of Pechmann and Frobenius[1] was modified a little and used for the synthesis of TTP. 10.7 g. of *p*-toluidine (0.1 mol.) in 15 ml. of water was diazotized by the addition of 6.9 g. of sodium nitrite (0.1 mol.) in 20 ml. of water and 25.1 g. of 35% hydrochloric acid (0.1 mol.) at 0°C. 5.1 g. of sodium (0.22 mol.) was dissolved in 150 ml. of methanol, and to this sodium methoxide solution 5.35 g. of *p*-toluidine (0.05 mol.) in 110 ml. of methanol was added. Then this methanolic solution was stirred, drop by drop, within half an hour to the aqueous soluion of *p*-toluenediazonium chloride. The yellow TTP precipitated was filtered and washed with cold ether. When the crude TTP was quickly recrystallized from cold ether, 5.5 g. of yellow crystals was obtained (16%). M. p. 84.5 — 85.0°C (decomp.) (literature :[1] 85.0°C).

When the ethereal solution of TTP was kept at −3°C for 36 hr., all the TTP were found to have decomposed. When TTP was added to acetone, benzene, ether or chloroform at room temperature, it quickly dissolved, with a rapid evolution of nitrogen. When TTP was added to chloroform, the decomposition was accompanied with a strong smell which resembled that of phenyl isocyanide. When the chloroform solution was viewed against pure chloroform in the infrared region, an absorption at 2220 $\mathrm{cm^{-1}}$ was observed; this may be ascribed to *p*-tolyl isocyanide.

Kinetic Procedure.—One gram of TTP was placed in a container attached to one end of a U-shaped tube, while 100 ml. of cumene was placed in a container 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°. This U-tube was attached to an evacuated system of a known volume with a mercury manometer. Then a water bath of a constant temperature (0.00, 15.00 or 25.80± 0.05°C) was raised so that the U-tube was immersed in the bath. By turning a cock, 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.

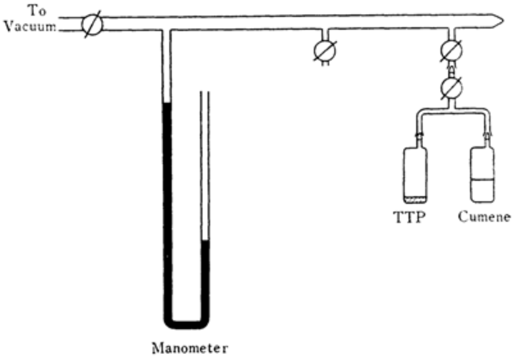

Fig. 4. Vacuum system used for kinetic and product studies.

Procedure for Product Studies.—The TTP 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 only peaks observed were those of toluene and cumene. The amount of toluene was determined by using benzene as the internal standard.

When the brown residue was recrystallized from cold petroleum ether, brownish yellow crystals of 1,3-di-*p*-tolyltriazene were obtained, while upon the evaporation of the filtrate crystals of 2,3-dimethyl-2,3-diphenylbutane (bicumyl) were obtained. The melting points and the infrared spectra of these two products were the same as those of authentic samples.

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

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