Possibility of the Intramolecularity of Triazene Rearrangement[1)]

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Synopsis. The mechanism for the ortho-rearrangement of diaryltriazenes still remains equivocal. An interesting result suggesting an intramolecular nature of the triazene rearrangement was obtained on the basis of the effect of concentration of added *N,N*-dimethylaniline in the ortho-rearrangement of 1,3-bis(4-methylphenyl)triazene (**1**). The ortho/para ratio for the rearrangement of 1,3-diphenyltriazene (**4**) tends to increase with an increase of the viscosity. The results are discussed on the basis of increasing nucleophilicity of free amine by H-bonding with dimethylaniline and favoring ortho-migration with viscosity, respectively.

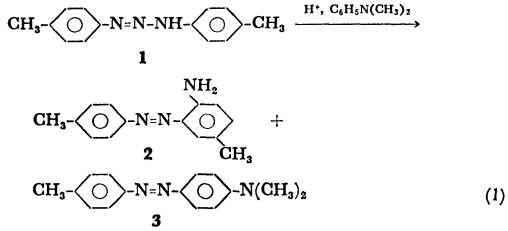
It is known that acid-catalyzed rearrangement of 1,3-diphenyltriazene to *p*-aminoazobenzene, accompanied by a small amount of *o*-isomer[2)] (Eq. 2), is intermolecular based on the trap of intermediary diazonium ion with phenols and dialkylanilines.[3)] However, as to the ortho-rearrangement at least, the possibility of intramolecular mechanism cannot be excluded.

Berezovskii *et al.*[4)] suggested that the ortho-rearrangement has an intramolecular character based on analogous yields for the rearrangement of 1,3-bis(3,4-dimethylphenyl)triazene in *p*-toluidine and in chlorobenzene, but their evidence is not definitive.

We attempted to clarify the mechanism of triazene rearrangement by the examination of the effects of the addition of *N,N*-dimethylaniline as a trapping agent for the intermediary diazonium ion during the rearrangement and also of the solvent effect on the ortho/para ratio of 1,3-diphenyltriazene. The results suggest the partial intramolecularity of the rearrangement.

Results and Discussion

Effect of N,N-*Dimethylaniline on 1,3-Bis(4-methylphenyl)-triazene Rearrangement.* 1,3-Bis(4-methylphenyl)-triazene (**1**) was rearranged in acidic ethanol, affording 2-amino-5,4′-dimethylazobenzene (**2**). In the presence of *N,N*-dimethylaniline (DMA) as a scavenger of diazonium ion, **1** gave 4-dimethylamino-4′-methylazobenzene (**3**) as well as the rearrangement product **2**.



(1)

A plot of the reciprocal of the initial concentration of added DMA ($1/[DMA]_0$) *vs.* a ratio of the yields of **2** to **3** (**2/3**) is shown in Fig. 1.

Assuming this rearrangement to be completely intermolecular, the ratio (**2/3**) must be zero, when

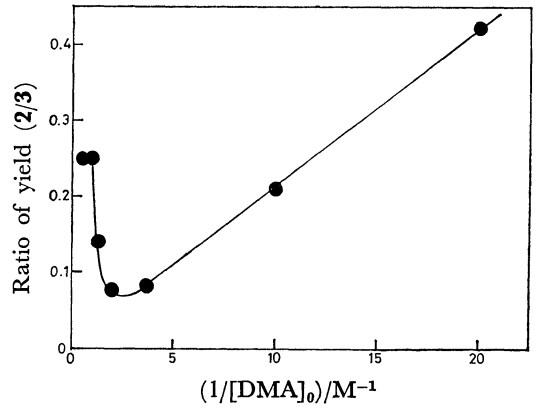


Fig. 1. Effect of *N,N*-dimethylaniline on the rearrangement of **1** in ethanol at room temperature.
The initial concentrations of reagents were: $[\mathbf{1}]_0$= 0.05 M, $[HCl]_0$=0.011 M.

$[DMA]_0$ is extrapolated to infinity. As shown in Fig. 1, the ratio decreases really until $[DMA]_0$ of 0.75 M (1 M=1 mol dm^{-3}), but with increasing $[DMA]_0$ over 0.75 M, the ratio increases to 0.25, which suggests an increase of intramolecular nature of the rearrangement at very high concentration of DMA.

The Goldschmidt mechanism[5)] in which protonated triazene reacts with anilines might explain the observed plot of the **2/3** ratio *vs.* $1/[DMA]_0$ (Fig. 1), but the mechanism requires that the analogous DMA-catalyses should operate with both rearrangement and DMA-coupling at high $[DMA]_0$. Hence the higher ratio of **2/3** at low $1/[DMA]_0$ cannot be explained.

The increase of intramolecular nature by increasing $[DMA]_0$ may be caused by increasing the nucleophilicity of $ArNH_2$ of intermediary $[ArNH_2 \cdot N\equiv \overset{+}{N}Ar]$ *via* hydrogen bonding $Ar\overset{\delta-}{N}H\cdots H\cdots \overset{\delta+}{N}Me_2Ph$. The diazo coupling reaction takes place between diazonium ion and free amine[6)] which exist in neutral and even weakly acidic media. In fact, the yield of **2** for the rearrangement of **1** ($[\mathbf{1}]_0$=0.05 M) in ethanol with $[HCl]_0$=0.005 M (37%) in the absence of DMA was found to be higher than those with $[HCl]_0$=

Table 1. Effect of *N,N*-dimethylaniline (DMA) on the rearrangement of 1,3-bis(4-methylphenyl)-triazene (**1**) in ethanol at room temperature[a)]

$[\mathbf{1}]_0$ (M)	$[DMA]_0$ (M)	Yield/%		Ratio of yields
		2	**3**	**2/3**
0.051	0	23	—	—
0.045	0.050	19	48	0.39
0.046	0.10	13	65	0.21
0.046	0.27	3.7	45	0.083
0.045	0.52	3.4	44	0.077
0.046	0.75	8.1	58	0.14
0.048	1.0	11	48	0.25
0.045	2.0	14	57	0.25

a) Initial concentration; $[HCl]_0$=0.011 M. Products other than **2** and **3** were toluene and *p*-toluene formed by decomposition.

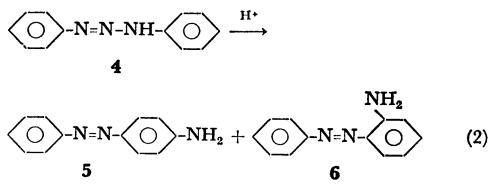
Table 2. Solvent effect on the rearrangement of 1,3-diphenyltriazene (**4**)[a] and 1,3-bis(4-methylphenyl)triazene (**1**)[b]

Solvent	Viscosity/cp		Dielectric constant	Rearr. of **4** Yield[c]/%		Ratio of yields	Rearr. of **1** Yield/%
	At 30 °C	At 30 °C	at 25 °C	**5**	**6**	**6/5**	**2**
Methanol	0.51		32.6	64	5.8	0.09	5
Ethanol	0.99	1.46	24.3	75	8.2	0.11	21
Propanol	1.72	2.89	19.7	74	—[e]	—	32
2-Propanol	1.77	3.26	18.3	73	10	0.14	33
1-Butanol	2.27	3.87	17.7	75	12	0.16	4[f]
2-Butanol	3.18	—	16.6	55	—[e]	—	33
t-Butyl alcohol	3.32	—	12.5	61	14	0.23	34
DG[d]	30[g]	—	31.7[h]	18	1.8[i]	0.10	3

a) Initial concentration; $[\mathbf{4}]_0=0.051$—0.052 M, $[HCl]_0=0.0054$ M. Reaction temp.; 30 °C. b) Initial concentration; $[\mathbf{1}]_0=0.046$—0.051 M, $[HCl]_0=0.011$ M. Reaction temp.; room temp. c) Duplicates gave similar results on the trend with viscosity effect, so that the average yields were shown here. d) Diethylene glycol. e) These yields could not be estimated because of the overlapping of the HPLC peaks of **6** and unknown product. f) A large amount of **1** was recovered. g) At 25 °C. h) At 20 °C. i) This yield was estimated after concentration of the solution of products by evaporating the solvent. However, the yield for DG is low because of the decomposition of triazene giving aniline and benzene (GLC analysis) so that the data are little reliable.

0.01 M (25%) and 0.02 M (15%). Ethanol, as in the case of HCl, may deactivate $ArNH_2$ by hydrogen bonding. The increase of nucleophilicity of $ArNH_2$ lowers the selectivity and raises the *o*/*p* ratio.

Solvent Effect in 1,3-Diphenyltriazene Rearrangement. 1,3-Diphenyltriazene (**4**) gives *p*- (**5**) and *o*-aminoazobenzene (**6**).[2] As shown in Table 2, satisfactory yields of rearrangement products were obtained except with 1-butanol and diethylene glycol. We expected that the ortho-rearrangement may occur *via* intramolecular process, especially in viscous solvents. Hence, **4** was rearranged in various solvents under



acidic conditions. The effect of viscosity on the ratio of ortho/para-was examined by estimating the ratio of the yields of ortho *vs.* para (**6**/**5**) (Table 2).

The ratio, **6**/**5**, or the trend for ortho migration tends to increase slightly with increasing viscosity of the solvent in going from methanol to *t*-butyl alcohol. The same tendency was also observed with the rearrangement of **1**, where the yield of **2** increased in going from methanol to **2**-propanol (Table 2).

This tendency for the ratio **6**/**5** and yields of **2** suggests that the triazene rearrangement has at least a partial contribution of intramolecularity. The increase of the ratio **6**/**5** and the yield of **2** may be caused by an increase of viscosity. In the reaction of diethylene glycol, the decomposition of triazene to aniline and benzene is remarkable; the yields of rearrangement products are so poor. Also the yield of rearrangement of **1** in 1-butanol was poor, a considerable amount of **1** being recovered.

Experimental

Melting points were measured by a Yanagimoto micro melting point apparatus and uncorrected. NMR spectra were recorded on a Hitachi R-24B NMR spectrometer using Me_4Si as an internal standard. The HPLC analysis was performed with a Yanagimoto L-1030 high pressure liquid chromatograph.

Materials. Triazenes were prepared from corresponding anilines by the method of Hartman *et al*;[7] 1,3-diphenyltriazene: mp 95—97.5 °C (lit,[7] 94—96 °C); NMR (CCl_4) δ 7.3 (m, 10H, ArH), 9.9 (s, 1H, NH); UV (EtOH) λ_{max} 353 nm (ε 1.98×10^4), 294 nm (0.74×10^4), 236 nm (1.69×10^4). 1,3-bis(4-methylphenyl)triazene: mp 119—120 °C (lit,[8] 118 °C); NMR (CCl_4) δ 2.28 (s, 6H, CH_3), 7.1 (dd, 8H, ArH), 9.5 (s, 1H, NH); UV (EtOH) λ_{max} 357 nm (ε 2.03×10^4), 292 nm (1.02×10^4), 238 nm (1.73×10^4). Solvents were of commercial guaranteed grade and purified by fractional distillation.

Effect of N,N-*Dimethylaniline on the Rearrangement of 1,3-Bis(4-methylphenyl)triazene (1).* An ethanolic solution (10 ml) of **1** (0.05 M) and *N*,*N*-dimethylaniline containing HCl (0.011 M) was allowed to stand at room temperature for 3 d, until **1** was consumed. One ml of the resulting solution was pipetted out and ethanol was added for dilution to a suitable concentration for HPLC analysis. The HPLC analysis was performed under the following conditions using Yanaco SA-I as a packing. A carrier solvent of hexane/THF (9/1 in vol.) was used at a flow rate of 40 ml/h. The products were identified by HPLC peaks in comparison with the authentic specimens.

Solvent Effect in 1,3-Diphenyltriazene (4) Rearrangement. Various solutions (10 ml) of **4** (0.05 M) containing HCl (0.005 M) were allowed to stand at 30 °C in a thermostat for 2 d, until **4** was consumed. In a similar manner as above, the products were identified and estimated by HPLC under the following conditions. Yanaco SA-I was used as a packing, and hexane/THF (7/3) was used at a flow rate of 90 ml/h. Products from propanol and 2-butanol contained a small amount of unknown product, which showed UV peaks (334 nm) different from *o*-aminoazobenzene, 4-(phenyldiazoamino)azobenzene (C_6H_5–N=N–NH–C_6H_4–N=N–C_6H_5) and *p*-[*p*-(phenylazo)phenylazoaniline (C_6H_5–N=N–C_6H_4–N=N–$C_6H_4NH_2$).

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