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# Triazene Rearrangement. III.[*1] A Kinetic Study of the Rearrangement of *N*-Methyldiaryltriazenes

Takashi YAMADA[*2]

*Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto*

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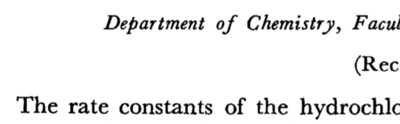
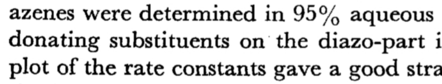
The rate constants of the hydrochloric acid-catalyzed rearrangement of *N*-methyldiaryltriazenes were determined in 95% aqueous ethanol in the presence of *N*-methylaniline. Electron-donating substituents on the diazo-part in triazene promoted the rearrangement. A Hammett plot of the rate constants gave a good straight line. The negative $\rho$-value ($-3.63$ at 30.0°C) and the large positive values of the entropy of activation suggested that the rate-determining step in this rearrangement is the dissociation of protonated triazene; this is in contrast with the case of the Friswell-Green mechanism. This theory was suppoted by such a solvent effect as that the rate decreased a little as the polarity of the solvent increased. The kinetic behavior of triazenes in the absence of *N*-methylaniline, and the incorporation of *N*-methyl-*o*-toluidine into the product in the rearrangement of 1-*p*-chlorophenyl-3-methyl-3-phenyltriazene (Id), were also discussed in connection with the above mechanism.

On the mechanism of the triazene rearrangement, several product studies1) have thus far been presented. As a result, Friswell-Green's mechanism2) prevails, though a few objections3) have been offered against it.



(1)

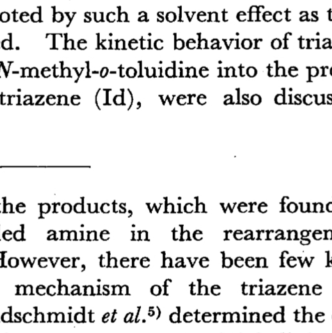


(2)

In our previous papers,4) Friswell-Green's mechanism was supported by the quantitative analyses of the products, which were found to contain the added amine in the rearrangement.

However, there have been few kinetic studies of the mechanism of the triazene rearrangement; Goldschmidt *et al.*5) determined the order of reaction in the rearrangement of 1,3-diphenyltriazene, but they could not clarify the details of the reaction mechanism. Yokojima6) insufficiently examined the effect of amines upon the reaction rate in ethanol.

In this paper, the author will report on the substituent effect, the solvent effect, and the thermodynamics of activation and will discuss the mechanism of the triazene rearrangement in more detail.



Ia—f

IIa—f

(3)

$$X = \begin{cases} a: p\text{-OCH}_3 & b: p\text{-CH}_3 & c: m\text{-CH}_3 \\ d: p\text{-Cl} & e: p\text{-COCH}_3 & f: p\text{-CN} \end{cases}$$

For this purpose, *N*-methyldiaryltriazene (I) was used, for in it 1,3-prototropy7) can not occur.

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[*2] Present address: Laboratory of Chemistry, Faculty of Science, Konan University, Okamoto, Higashinada-ku, Kobe.

1) a) For a recent review, see H. J. Shine, "Aromatic Rearrangements," Elsevier Publishing Co., Amsterdam, London and New York (1967), p. 212. b) E. Rosenhauer, *Z. angew. Chem.*, **40**, 575 (1927). c) E. Rosenhauer and H. Unger, *Ber.*, **61**, 392 (1928). d) H. V. Kidd, *J. Org. Chem.*, **2**, 198 (1937). e) K. Clusius and H. R. Weisser, *Helv. Chim. Acta*, **35**, 1524 (1952).

2) R. J. Friswell and A. G. Green, *J. Chem. Soc.*, **47**, 917 (1885); *ibid.*, **49**, 746 (1886).

3) a) H. Goldschmidt, *Ber.*, **24**, 2317 (1891). b) H. Goldschmidt and B. Bardach, *Ber.*, **25**, 1347 (1892). c) V. M. Berezovskii and L. S. Tul'chinskaya, *J. Gen. Chem. USSR*, **31**, 2587, 3371 (1961); *ibid.*, **32**, 846 (1962).

4) a) R. Goto, T. Yamada and A. Sera, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **87**, 198 (1966). b) T. Yamada, R. Goto, A. Kaji and S. Kurabayashi, *ibid.*, **90**, 207 (1969).

5) a) H. Goldschmidt and R. U. Reinders, *Ber.*, **29**, 1369, 1899 (1896). b) H. Goldschmidt and M. Salcher, *Z. physik Chem.*, **29**, 89 (1899). c) H. Goldschmidt, S. Johnsen and E. Overwien, *ibid.*, **110**, 251 (1924).

6) N. Yokojima, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **31**, 100, 109 (1928).

7) a) M. M. Shemyakin, V. I. Maimind and E. Gomes, *J. Gen. Chem. USSR*, **27**, 1906 (1957). b) V. C. Farmer, R. L. Hardie and R. H. Thomson, "Hydrogen Bonding," Pergamon Press, N. Y. (1959), p. 475. c) T. Mitsuhashi and O. Simamura, *Chem. & Ind.*, **1964**, 578.

## Results

**Reaction in Ethanol.** The rearrangement of triazenes (Ia—f) was carried out in 95% aqueous ethanol in the presence of hydrochloric acid; the first-order rate plots of the reaction are shown in Figs. 1 and 2. The line for Ib ($X=p$-$CH_3$) is linear, whereas the line for Ia ($X=p$-$OCH_3$) is concave and the others are convex. Yokojima[6] observed a similar curve for the rearrangement of 1,3-diphenyltriazene in ethanol. This behavior of the lines can be ascribed to the difference in basicity between triazenes (I) and aminoazobenzenes (II), for the first-order plots became linear when the reaction was carried out in the presence of N-methylaniline, which seemed to be a stronger base than either Ia—f or IIa—f (Fig. 3). Consequently, the curves of Figs. 1 and 2 suggest that, regarding basicity, Ia>IIa, Ib≑IIb, and I<II for the others.

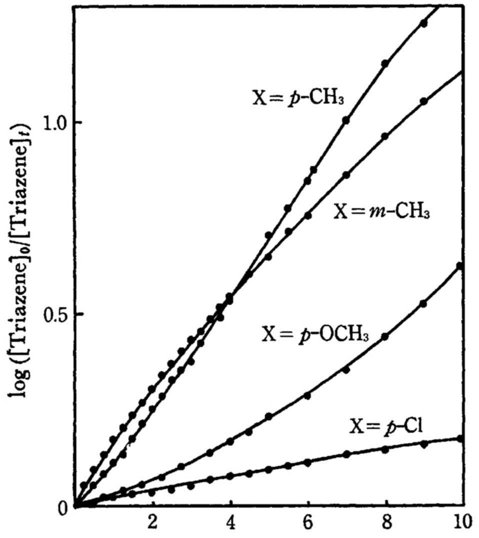


Fig. 1. First-order plots for the rearrangement of triazenes (Ia—d) in 95% aqueous ethanol at 30.0°C.
[Triazene]$=5.0\times10^{-3}$ M, [HCl]$=0.5\times10^{-3}$ M

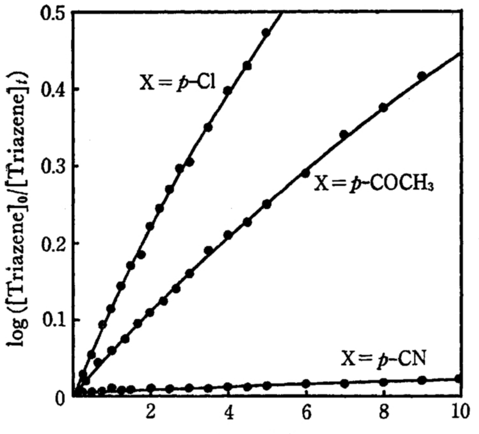


Fig. 2. First-order plots for the rearrangement of triazenes (Id—f) in 95% aqueous ethanol at 30.0°C.
[Triazene]$=5.0\times10^{-3}$ M, [HCl]$=2.5\times10^{-3}$ M

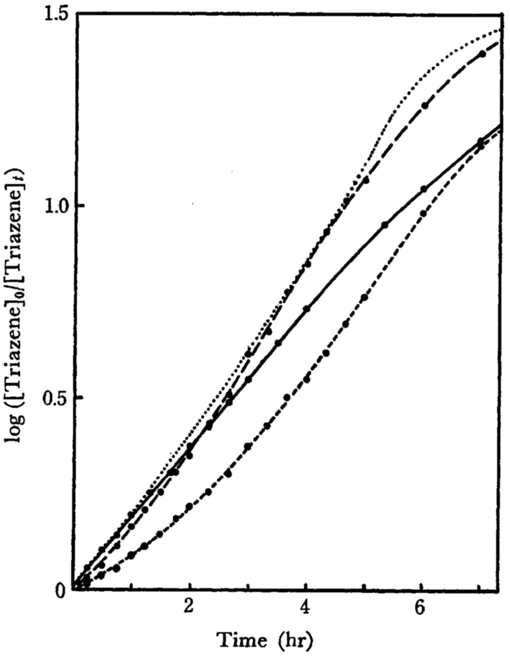


Fig. 3. First-order plots for the rearrangement of triazene (Ia) in the presence of various quantity of N-methylaniline.
[Triazene]$=5.0\times10^{-3}$ M, [HCl]$=1.0\times10^{-3}$ M
[N-Methylaniline] = 0 (- - -), $2.5\times10^{-3}$ M (— —), $5.0\times10^{-3}$ M (……), $10\times10^{-3}$ M (——)

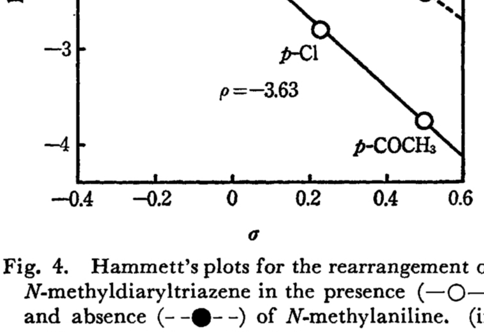


Fig. 4. Hammett's plots for the rearrangement of N-methyldiaryltriazene in the presence (—○—) and absence (- -●- -) of N-methylaniline. (in 95% aq. EtOH, at 30.0°C).

In Figs. 1 (except for Ia) and 2, it is qualitatively shown that the rearrangement is accelerated by the electron-donating substituents on the diazo-part of triazenes. A Hammett plot of the initial rate constants also shows it (Fig. 4). This acceleration is against the expectation from the mechanism proposed by Friswell and Green, in which the rate-determining step is the *C*-coupling reaction (Eq. (2)).

It is noteworthy that the initial rate of the rearrangement of Ia in the absence of *N*-methylaniline was lower than that of Ib and Ic, and that a Hammett plot was concave (Fig. 4), whereas the initial rate of Ia increased upon the addition of *N*-methylaniline to become greater than the rates of Ib and Ic in the presence of the amine (Figs. 3 and 4).

**Rearrangement in the Presence of *N*-Methylaniline.** The first-order rate plot was made linear by the addition of *N*-methylaniline of twice as much molar quantity as triazenes, even in the rearrangement of Ia, which may be the strongest base among the Ia—f and IIa—f (Fig. 3). Besides, the presence of the amine may favorably exclude the variation in the relative rate because of the difference in the basicities among I's or among II's, and prevent the decomposition of triazenes.[3)]

The rearranaement of I in ethanol containing *N*-methylaniline in the presence of hydrochloric acid was a second-order reaction; *i.e.*, it was first-order with respect to triazene and to the acid (Table 1). The same is true for the case of 1,3-diphenyltriazene in aniline.[5)]

TABLE 1. THE EFFECT OF ACID CONCENTRATION ON THE RATE CONSTANTS IN THE REARRANGEMENT OF 1-*p*-ANISYL-3-METHYL-3-PHENYLTRIAZENE*
(in 95% aq. EtOH, at 40.0°C)

| [HCl]×10⁴ (M) | $k\times10^5$ (sec$^{-1}$) | $k'$ (*l*/mol·sec) |
|---|---|---|
| 1.25 | 4.41 | 0.353 |
| 2.50 | 8.76 | 0.350 |
| 5.00 | 17.4 | 0.349 |
| 10.00 | 33.5 | 0.335 |

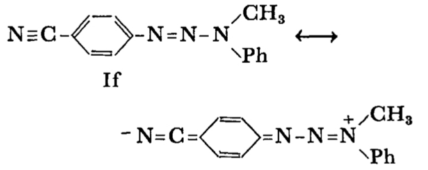
* [Triazene]=5.0×10⁻³ M
[*N*-Methylaniline]=1.0×10⁻² M, $k'=k/$[HCl]

TABLE 2. RATE CONSTANTS FOR THE REARRANGEMENT OF *N*-METHYLDIARYLTRIAZENES IN 95% AQUEOUS ETHANOL CONTAINING *N*-METHYLANILINE AT VARIOUS REACTION TEMPERATURES*

| Triazene | Substituent X | $k'\times10^2$ (*l*/mol·sec) 30.0°C | 40.0°C | 50.0°C |
|---|---|---|---|---|
| Ia | *p*-$CH_3O$ | 11.3 | 34.9 | 99.9 |
| Ib | *p*-$CH_3$ | 4.15 | 14.7 | 49.3 |
| Ic | *m*-$CH_3$ | 2.21 | 8.47 | 29.1 |
| Id | *p*-Cl | 0.157 | 0.650 | 2.46 |
| Ie | *p*-$COCH_3$ | 0.0173 | 0.105 | 0.408 |
| If | *p*-CN | — | 0.0109 | — |

* [Triazene]=5.0×10⁻³ M
[*N*-Methylaniline]=1.0×10⁻² M

Table 2 shows that electron-donating substituents on the diazo-part of triazene promote the rearrangement. A Hammett plot of the rate constants at 30.0°C gives a good straight line (Fig. 4, $\rho=-3.63$, $r=0.999$). In the plot of the rate constants at 40.0°C against $\sigma$, the point for *p*-CN deviated from a straight line. This deviation may be attributed to the fact that the protonation of triazene may be inhibited by such additional conjugation as that of III in the ground state of triazene (If).


If

III

(4)

Table 3 summarizes the activation parameters calculated from the values in Table 2. It is interesting that the entropies of activation ($\Delta S^{\neq}$) were large positive values.

TABLE 3. ACTIVATION PARAMETERS FOR THE REARRANGEMENT OF *N*-METHYL-DIARYLTRIAZENES IN 95% AQUEOUS ETHANOL

| Triazene | Substituent X | $E_a$ kcal/mol | $\Delta S^{\neq}$ (40°C) e.u. |
|---|---|---|---|
| Ia | *p*-$CH_3O$ | 21.2 | 5.0 |
| Ib | *p*-$CH_3$ | 24.1 | 12.5 |
| Ic | *m*-$CH_3$ | 25.1 | 14.6 |
| Id | *p*-Cl | 26.8 | 14.9 |
| Ie | *p*-$COCH_3$ | 30.7 | 23.7 |

TABLE 4. THE INFLUENCE OF WATER CONTENT IN AQUEOUS ETHANOL ON THE RATE CONSTANTS IN THE REARRANGEMENT OF 1-*p*-ANISYL-3-METHYL-3-PHENYLTRIAZENE*
(at 40.0°C)

| $H_2O$ (vol%) | $k'$ (*l*/mol·sec) |
|---|---|
| 2.5 | 0.362 |
| 5.0 | 0.349 |
| 10.0 | 0.320 |
| 20.0 | 0.295 |

* [Triazene]=5.0×10⁻³ M
[*N*-Methylaniline]=1.0×10⁻² M
[HCl]=5.0×10⁻⁴ M.

Further, the rates were measured in ehtanol containing various amounts of water; a rate decrease was observed with the increase in the polarity of the solvent (Table 4).

**Competition between *N*-Coupling and *C*-Coupling.** In the preparation of triazene (I),

TABLE 5. COUPLING PRODUCTS OF SUBSTITUTED BENZENEDIAZONIUM CHLORIDES AND *N*-METHYLANILINE IN WATER

| Substituent | Total yield* % | Ratio Triazene (I) | : Aminoazobenzene (II) |
|---|---|---|---|
| $p$-OCH$_3$ | 16.2 | >95 | —** |
| $p$-CH$_3$ | 47.6 | 98 | 2 |
| $m$-CH$_3$ | 65.8 | 97 | 3 |
| $p$-Cl | 76.6 | 97 | 3 |
| $p$-COCH$_3$ | 91.7 | 96 | 4 |
| $p$-CN | 91.9 | 96 | 4 |

* not optimum yield.
** II was not detected by TLC.

it was observed by thin-layer chromatography (TLC) that the crude products contained a small amount of aminoazo compounds (II). Therefore, in order to clarify the competition between *C*-coupling and *N*-coupling, the II content in the crude products was examined in the reaction of aryldiazonium with *N*-methylaniline (Table 5) (Eq. (5)).

The total yield of products increased with the electron-withdrawing property of the substituents, as was expected.[8] The formation of only a small amount of II showed that *N*-coupling is much more rapid than *C*-coupling. The introduction of the electron-withdrawing substituent resulted in a small but appreciable increase in the ratio of II to I. When the kinetic results in Table 2 are taken into account, it seems that the formation of II may be not through the rearrangement of triazene, but by a direct *C*-coupling competing with *N*-coupling.

**Incorporation of Amine in the Rearrangement.** When triazene (Id) was rearranged with hydrochloric acid in the presence of 1 equiv. of *N*-methyl-*o*-toluidine (IV), two products were detected by TLC: IId, the product expected from Id, and V, expected from the incorporation of the added amine (IV) (Eq. (6)).

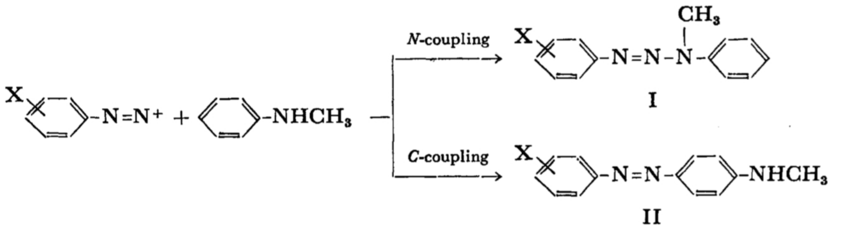
The fact that the yield of V was 56% evidently shows a very efficient incorporation of the added amine into the product and, thus, the intermolecular aspect of this reaction.

It is interesting to note that the ratio IId/V (33/67) roughly agrees with the ratio of the incorporation of *o*-toluidine into the amine-part of the products in the reaction showin in Eq. (7)(35/65).[4]

## Discussion

On the basis of the above results, it seems reasonable to assume as follows regarding the rearrangement of *N*-methyldiaryltriazene:

(1) The reaction process consists of three steps, in accordance with Friswell-Green's mechanism on the rearrangement of 1,3-diphenyltriazene: the protonation of triazene, the dissociation of the



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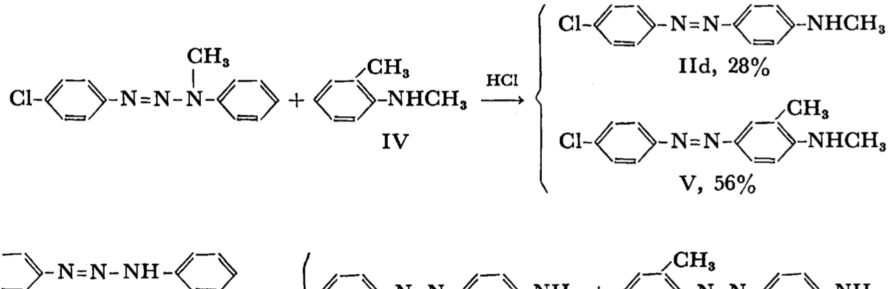

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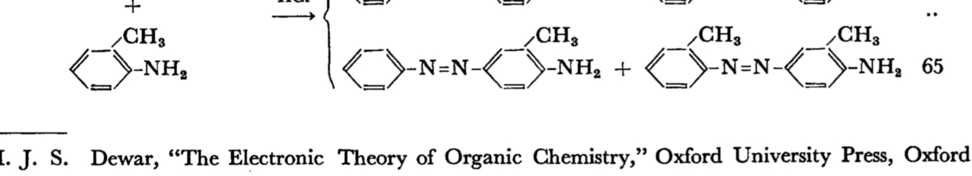

(7)

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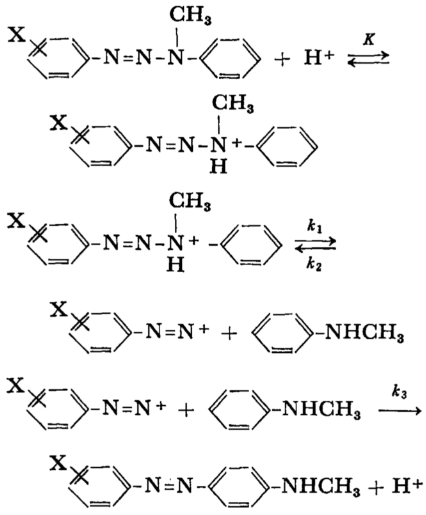
[8] M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, Oxford(1949), p. 183.

protonated triazene to the diazonium ion and amine, and the subsequent *C*-coupling of those moieties.



(2) However, the negative $\rho$-value (Fig. 4) and the large positive entropies of activation (Table 3) show that, in contrast with Friswell-Green's mechanism for 1,3-diphenyltriazene, the rate-determining step in the rearrangement of *N*-methyldiaryltriazene (I) is not the *C*-coupling step but the dissociation step of the protonated triazene to the diazonium ion and amine, *i.e.*, $k_1 < k_3 \ll k_2$. Although a negative $\rho$-value may also be expected from the substituent effect in the protonation of triazene, the protonation is probably not rate-determining, for it is reasonably assumed to be much more rapid than the dissociation of protonated triazene. If the protonation of triazene were the rate-determining step, $\Delta S^{\neq}$ might be expected to have a negative value.

According to Ingold's criterion,[9] the above consideration is supported by the solvent effect; the increase in the solvent polarity resulted in a small decrease in the rate (Table 4).

(3) As has been remarked above, unusual behavior was observed in the rate plot of the rearrangement of Ia in the absence of *N*-methylaniline (Figs. 1 and 3), and a Hammett plot of the initial-rates was concave (Fig. 4). These results may be interpreted as follows.

In the rearrangement of Ia in the absence of *N*-methylaniline, the *C*-coupling of diazonium with amine may be the rate-determining step (*i.e.*, $k_3 < k_1 \ll k_2$), whereas in the rearrangemnet of Ic—f the rate-determining step may be the dissociation of protonated triazene, even in the absence of the amine ($k_1 < k_3 \ll k_2$) and Ib may have an intermediate character. Such a change in the rate-determining step may cause the curve of a Hammett plot to be concave.

The increase in the basicity of triazene caused by the electron-donating substituent undoubtedly results in the rate decrease. The difference in $\rho$-values shown in Fig. 4 ($-3.63$ in the presence of *N*-methylaniline and $-2.98$ in its absence) is probably due to this effect. However, the decrease in Ia is too large to be ascribed to the same effect.

The enhancement of the initial-rate observed when a small quantity of *N*-methylaniline was added may be because the rate-determining step lies in the *C*-coupling.

(4) In our previous papers,[4] we supported Friswell-Green's mechanism because, judging from the results of the product analysis, the rate-determining step of the triazene rearrangement seemed to be the *C*-coupling reaction.

However, the efficient incorporation of the added amine, *N*-methyl-*o*-toluidine, into products was also observed in the rearrangement of Id in which the rate-determining step was clearly, on the basis of the kinetic results, the dissociation of protonated triazene. That is, the incorporation might well occur if the relative rate were $k_3 \ll k_2$ whether the rate-determining step is the *C*-coupling or the dissociation of protonated triazene. Therefore, on the rearrangement of the 1,3-diphenyltriazene previously discussed on the basis of only the product studies of the incorporation reaction,[4] further kinetic study is desirable.

## Experimental*3

**Materials.** *The triazenes (I)* were prepared by the reaction of the corresponding aryldiazonium chlorides and *N*-methylaniline by the usual procedure;[10] they were purified by several recrystallizations from ethanol. The triazene (If) was purified by elution chromatography over activated alumina, using benzene as an eluent, and by recrystallization from ethanol.
Ia: mp 59.5—60.0°C (lit,[11] 59.8—60.2°C, lit,[12] 61°C), Ib: mp 66—67°C (lit,[11] 67—67.8°C, lit,[12] 66.5—68°C), Ic: mp 63.5—64.5°C (lit,[12] 67°C), Id: mp 87—88°C (lit,[11] 86.7—88.1°C), Ie: mp 85—85.5°C, bright yellow needles;

Found: C, 70.88; H, 6.11; N, 16.42%. Calcd for $C_{15}H_{15}N_3O$: C, 71.13; H, 5.97; N, 16.59%.
If: mp 120—120.5°C, bright yellow prisms;

Found: C, 71.36; H, 5.10; N, 23.70%. Calcd for $C_{14}H_{12}N_4$: C, 71.17; H, 5.12; N, 23.71%.

*Aminoazobenzene Derivatives (II).* These were prepared by the condensation of nitrosobenzene derivatives with

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[9] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y. (1953), p. 345.

*3 All melting points are uncorrected. A Hitachi Perkin-Elmer 139 UV-VIS spectrophotometer was used for the ultraviolet and visible spectrophotometric measurements.

[10] W. W. Hartman and J. B. Dickey, "Organic Syntheses," Coll. Vol. II, p. 163 (1943).

[11] R. F. Day, T. W. Campbell and G. M. Coppinger, *J. Am. Chem. Soc.*, **73**, 4687 (1951).

[12] L. Hunter, *J. Chem. Soc.*, **1937**, 320.

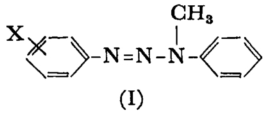
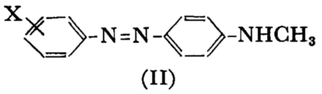
TABLE 6. THE ANALYTICAL DATA AND PHYSICAL CONSTANTS OF 4-(*N*-METHYL)-AMINOAZOBENZENES (II)

| Aminoazo-benzene | Preparative method | Mp °C | Analysis (calcd) | | |
|---|---|---|---|---|---|
| | | | C% | H% | N% |
| IIa | B | 147—148 | 69.64 | 6.41 | 17.45 |
| | | | (69.69) | (6.27) | (17.42) |
| IIb | A | 104.5—105.5 | 74.36 | 6.89 | 18.47 |
| | | | (74.64) | (6.71) | (18.65) |
| IIc | B | 111.5—112.5 | 74.58 | 6.80 | 18.88 |
| | | | (74.64) | (6.71) | (18.65) |
| IId | A | 124—125 | 63.83 | 4.83 | 17.24 |
| | | | (63.54) | (4.92) | (17.10) |
| IIe | B | 170—171 | 70.86 | 6.26 | 16.62 |
| | | | (71.13) | (5.97) | (16.59) |
| IIf | A | 192.5—193.5 | 71.37 | 5.10 | 23.91 |
| | | | (71.17) | (5.12) | (23.71) |

TABLE 7. THE ANALYTICAL DATA AND PHYSICAL CONSTANTS OF X-SUBSTITUTED-PHENYLAZO-*N*-METHYLFORMANILIDES

| Substituent X | Mp °C | Analysis (calcd) | | |
|---|---|---|---|---|
| | | C% | H% | N% |
| $p$-$CH_3$ | 111.8—112.6 | 71.39 | 6.12 | 16.67 |
| | | (71.12) | (5.97) | (16.59) |
| $p$-Cl | 148—149 | 61.19 | 4.45 | 15.45 |
| | | (61.43) | (4.42) | (15.35) |
| $p$-CN | 156—157 | 68.43 | 4.68 | 21.15 |
| | | (68.17) | (4.58) | (21.20) |

TABLE 8. ELECTRONIC SPECTRAL DATA OF TRIAZENES (I) AND AMINOAZOBENZENES (II) (Solvent : EtOH)

| Substituent X | <br>(I) | | | <br>(II) | |
|---|---|---|---|---|---|
| | $\lambda_{max}$ mμ ($10^{-4}\varepsilon$) | | | $\lambda_{max}$ mμ ($10^{-4}\varepsilon$) | |
| $p$-$CH_3O$ | 236 (1.47) | 296 (1.12)<br>308 (1.05) | 351 (1.91) | 251 (1.03) | 401 (3.04) |
| $p$-$CH_3$ | 237 (1.39) | 296 (0.91) | 345 (2.00) | 253 (0.98) | 401 (2.86) |
| $m$-$CH_3$ | 236 (1.69) | | 343 (1.87) | 253 (0.97) | 402 (2.82) |
| $p$-Cl | 236 (1.73) | 295 (0.97) | 346 (2.14) | 266 (0.83) | 411 (3.03) |
| $p$-$COCH_3$ | 241 (1.62) | | 365 (2.82) | 279 (1.17) | 438 (3.22) |
| $p$-CN | 241 (1.91) | | 358 (2.60) | 271 (1.22) | 440 (3.32) |

*p*-amino-*N*-methylformanilide, followed by hydrolysis[13] (Method A) or by the rearrangement of triazenes (Method B). The II derivatives were then purified by several recrystallizations from ethanol.

The analytical data and physical constants of II and a few *N*-formyl-derivatives of II are summarized in Tables 6 and 7. The electronic spectral data of I and II are summarized in Table 8.

*4′-Chloro-3-methyl-4-N-methylaminoazobenzene (V).* This was prepared by the reaction of *p*-chlorobenzenediazonium chloride with *o*-methyl-*N*-methylaniline (bp 104—107°C/28 mmHg):[14] this mixture was stirred at room temperature for several hours without any isolation of the triazene initially produced; the dark-red material precipitated was recrystallized from ethanol containing alkali to give pure V as red needles with a melting point of 138.2—138.8°C. UV, $\lambda_{max}$ ($\varepsilon \times 10^{-4}$) 272 mμ (1.11), 412 mμ (3.02) (in ethanol).

Found: C, 64.95; H, 5.47; N, 16.27%. Calcd for $C_{14}H_{14}N_3Cl$: C, 64.74; H, 5.43; N, 16.18%.

**Kinetic Measurements.** A little less than 95 m*l* of an ethanol solution containing $5.0 \times 10^{-4}$ mol of tri-

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[13] *cf.* F. Witt, *Ber.*, **45**, 2380 (1912).

[14] This compound was prepared according to the procedure of R. M. Roberts and P. J. Vogt; R. M. Roberts and P. J. Vogt, "Organic Syntheses," Coll. Vol. IV, p. 420 (1963).

azene and $1.0\times10^{-3}$ mol of *N*-methylaniline was placed in a 100-m*l* measuring flask covered with aluminum foil in order to exclude all light; it was then kept at an appropriate reaction temperature in a thermostated water bath. After about an hour, 5 m*l* of aqueous hydrochloric acid was pipetted into this solution, and the entire solution was made up to volume with ethanol. Aliquots (1 m*l* each) were removed at intervals and put into 10-m*l* measuring flasks containing a sodium hydroxide solution (1 m*l*) in concentrations enough to neutralize the catalytic acid. The solution was made up to volume with ethanol, and, further, the solution was diluted ten times with ethanol to be used as the sample for the optical density measurements. All these samples were kept in the dark.

The optical densities were measured at two different wavelengths, 343—365 m$\mu$ ($\lambda_{\max}$ for I) and 400—440 m$\mu$ ($\lambda_{\max}$ for II) (see Table 8); the data were then treated in the manner previously described[15] to give the concentrations of the triazene remaining and of the aminoazobenzene produced. The reaction rate constants were evaluated by the graphical method. A typical example is shown in Fig. 5. As the rate constants of the disappearance of I were found to agree with those of the formation of II, the former are summarized in Table 2.

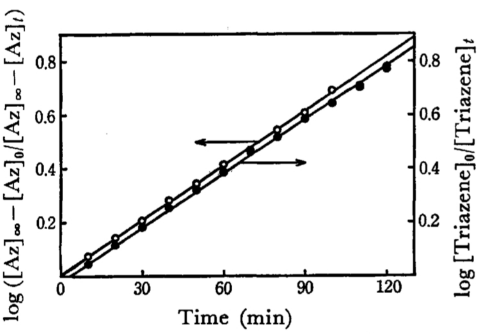

Fig. 5. Typical first-order plots for the rearrangement of triazene (Ib) in 95% aqueous ethanol at 50.0°C. (Az=aminoazobenzene (IIb)) [Triazene]$=5.0\times10^{-3}$ M, [HCl]$=0.5\times10^{-3}$ M, [*N*-Methylaniline]$=10\times10^{-3}$ M

**Competition between *N*-Coupling and *C*-Coupling.** A solution of the diazonium salt prepared in the usual way from 0.01 mol of the corresponding aniline (in 15 m*l* of water), 3 m*l* of the concentrated hydrochloric acid, and 0.67 g of sodium nitrite (in 3.5 m*l* of water at 0— −2°C was added to a cold solution of *N*-methyl-aniline (1.07 g, 0.01 mol) in 6% aqueous hydrochloric acid (6 m*l*). The mixture was stirred for 10 min at −3— −5°C. Then, to this mixture, a solution of 4.5 g (0.033 mol) of crystalline sodium acetate dissolved in 10 m*l* of water was added, and the stirring was continued for 30 min, keeping the temperature below 0°C. The precipitate of triazene produced was filtered, washed with cold water, and then dried over calcium chloride in a desiccator for a day.

The ratios of I to II in the products not still purified were obtained by the spectrophotometric method described above (Table 5).

**Incorporation of *N*-Methyl-*o*-toluidine in the Rearrangement of Triazene (Id).** Id (248 mg, $10^{-3}$ mol) was rearranged by the action of 0.1 N aqueous hydrochloric acid (2 m*l*) in ethanol (50 m*l*) containing *N*-methyl-*o*-toluidine (121 mg, $10^{-3}$ mol) at 40°C for several days. After TLC showed that all the triazene had been consumed, the reaction mixture was neutralized with a 0.05 N aqueous sodium hydroxide solution (5 m*l*). TLC (Merck silica gel G, *n*-hexane-benzene (3 : 1)) showed two main products, namely, IId and V, and a trace of two products which might be *ortho*-rearranged products. 2′,3-Dichloro-4-aminoazobenzene (VI) was added to the solution as an internal standard. Each component was separated by TLC on silica gel and was extracted with ethanol. The yield was determined from the intensity of the maximum absorption of each extract in an electronic spectrum. The extinction coefficients used were: Id $\varepsilon_{411\,\mathrm{m}\mu}=30300$, V $\varepsilon_{412\,\mathrm{m}\mu}=30200$, and VI $\varepsilon_{397\,\mathrm{m}\mu}=25700$ (in ethanol).

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[15] For example, see H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley & Sons, Inc., New York (1962), p. 557.