Photobenzidine Rearrangements. IV. Products from Photolysis of 1,4-Diethyl-1,4-diphenyl-2-tetrazene. Spin Trapping of *N*-Ethylanilino and *N*-Methylanilino Radicals[1-3]

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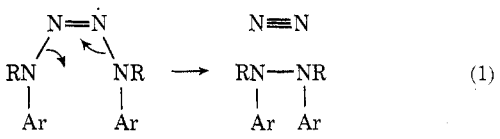
On irradiation at 350 nm in cyclohexane at 18° 1,4-diethyl-1,4-diphenyl-2-tetrazene (**1b**) gave 47% *N,N'*-diethylhydrazobenzene (**3b**), 20% *N*-ethylaniline (**4b**), 6% *N,N'*-diethyl-*N*-phenyl-*p*-phenylenediamine (**5b**), and 6% 3-(*N*-ethylamino)-9-ethylcarbazole (**17**). Compound **17** was shown to be formed from irradiation of **5b**. Compound **5b** is the *p*-semidine corresponding with rearrangement of **3b**, although it is most likely an initial photoproduct from **1b**. Irradiation of **1b** and also the *N,N'*-dimethyl analog (**1a**) in the presence of the spin traps, nitrosobenzene, and perdeuterio-, 3,5-dideuterio-, 3,5-dichloro-, and 3,5-di-*tert*-butylnitrosobenzene led to successful trapping of the *N*-ethyl- and *N*-methylanilino radicals. Data from esr spectra are presented. Trapping with methylene *tert*-butyl nitrone and methylene-d_2 *tert*-butyl nitrone led to unidentifiable esr spectra. CIDNP signals could not be found in the irradiation of **1b**.

The photochemistry of 1,4-dialkyl-1,4-diaryl-2-tetrazenes (**1**) is linked to that of *N,N'*-dialkylhydrazobenzenes (**3**). Photorearrangement of *N,N'*-dimethylhydrazobenzenes to *o*- and *p*-semidines occurs readily.[4,5] Corresponding 1,4-dimethyltetrazenes give *N,N'*-dimethylhydrazobenzenes and their rearrangement products when irradiated.[2,5] In particular, 1,4-dimethyl-1,4-diphenyl-2-tetrazene (**1a**) gave *N,N'*-dimethylhydrazobenzene (**3a**) and *N,N'*-dimethyl-*N*-phenyl-*p*-phenylenediamine (the *p*-semidine) (**5a**), but **5a** appeared to be a primary photoproduct.[5] The mechanism of formation of **3a** and **5a** from **1a** and the mechanism of photobenzidine rearrangements are not known. The reactions in all likelihood involve free radicals. Nelsen has recorded esr spectra of *N*-*tert*-butylarylamino radicals from the photolysis of 1,4-diaryl-1,4-di-*tert*-butyl-2-tetrazenes at low temperatures, but final products were not given.[6] Esr spectra of dialkylamino[7] and *N*-acetylmethylamino[8] radicals have been recorded in irradiations of appropriate tetrazenes at −90°, and the kinetics of decay of dialkylamino radicals produced by photolysis of tetraalkyltetrazenes at low temperatures have been reported.[9] Bridger has shown that the same products are obtained from the photolysis of 1,4-di(2-naphthyl)-1,4-diphenyl-2-tetrazene as from the thermolysis of this tetrazene and the oxidation of *N*-phenyl-2-naphthylamine, and concludes that diarylamino radicals are involved in all cases.[10] Further, irradiation of **1a** gave not only **3a** and **5a** but also *N*-methylaniline (**4a**),[5] and there is little doubt that the formation of **4a** is a radical reaction. In spite of these substantial diagnostic evidences, it has not been shown directly that hydrazobenzenes and semidines (*e.g.*, **3a** and **5a**) are formed by recombination of *N*-alkylanilino radicals when tetrazenes such as **1a** are photolyzed. In particular, the hydrazobenzenes (*e.g.*, **3a**) could be formed by a concerted process from the first-formed *cis*-tetrazene (eq 1). There is, indeed, a suggestion that, in



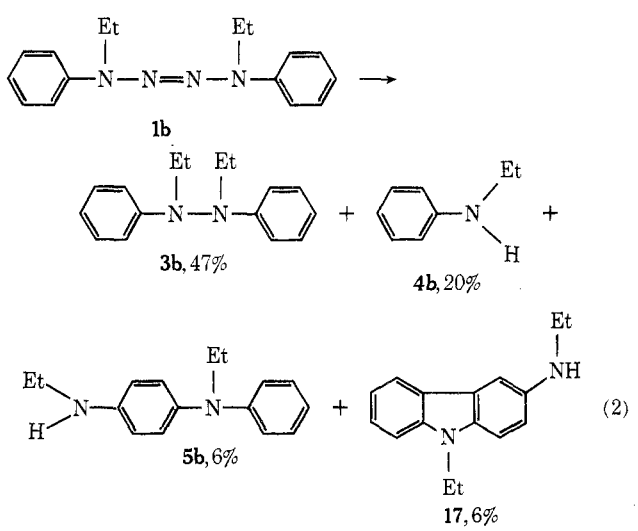
(1)

the irradiation of tetraalkyltetrazenes, the *cis*-tetrazene is the photoproduct and is the thermal source of dialkylamino radicals.[9] Our own spectroscopic work with the photodecomposition of 1,4-dimethyl-1,4-diaryl-2-tetrazenes, in which clean isosbestic points are recorded,[2] suggests that an intermediate is not involved, but the summation of these situations is that the details of product formation are not yet known.

In an attempt to clarify this problem we set out to show by the spin-trapping technique that radicals were formed under our conditions of photolyzing tetrazenes. Furthermore, we set out with **1b** to look, *via* the multiplet CIDNP effect, for *direct* evidence of radical participation in the formation of **3b**. The latter quest has proved negative: neither we nor others[11] were able to detect CIDNP signals in the photolysis of **1b**. The former quest was successful, and we are able to report our spin-trapping work with **1a** and **1b**, and on the products formed from the photodecomposition of **1b**.

Results and Discussion

Products. The photodecomposition of **1b** is summarized in eq 2. The products were isolated by column chromatog-



(2)

raphy and identified by comparison with authentic compounds. The *p*-semidine (**5b**) and isomeric *o*-semidine (**6b**) were synthesized so as to leave no doubt of the identity of **5b** as the photorearrangement product; **5b** was also characterized by its benzenesulfonyl derivative (**11**), mp 76–77°. Nmr data for these and other compounds are given in Table I. Earlier work[2,5] indicates that **5a**, the dimethyl analog of **5b**, is an initial[12] product in the photolysis of **1a**. We feel that this is probably true of **5b**, too, and, indeed, irradiation of **3b** alone, under the same conditions as irradiating **1b**, resulted in no change in **3b**. The

Table I
Nmr Data

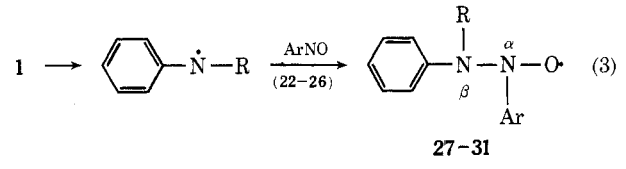
Compd	Solvent	Spectrum pattern[a]
1b	*b*	1.23 (t, 6), 4.12 (q, 4), 7.12 (m, 10)
2a	*b*	2.85 (s, 3), 3.33 (s, 2), 6.82 (m, 5)
2b	*b*	1.05 (t, 3), 3.33 (q, 2), 3.47 (s, 2), 6.9 (m, 5)
3b	*b*	1.22 (t, 6), 3.45 (q, 4), 6.75 (m, 10)
4b	*b*	1.97 (t, 3, J = 7), 3.04 (q, 2, J = 7), 3.27 (s, 1), 6.95 (m, 5)
5b	*b*	1.15 (t, 6), 3.06 (q, 2), 3.31 (s, 1), 3.61 (q, 2), 6.83 (m, 9)
6b	*c*	1.1, 1.17 (2 t, 6), 3.1 (q, 2), 3.55 (q, 2), 4.1 (s, 1), 6.95 (m, 9)
7	*c*	2.17 (s, 3), 7.2 (m, 10), NH[d]
8	*b*	1.09, 1.26 (2 t, 6), 1.76 (s, 3), 3.68, 3.83 (q, 4), 7.15 (m, 9)
9	*b*	1.11 (t, 3), 1.85 (s, 3), 3.75 (q, 2), 5.63 (s, 1), 7.15 (m, 9)
10	*c*	1.20 (t, 3, J = 7), 2.15 (s, 3), 3.77 (q, 2, J = 7), 7.18 (m, 9) NH[d]
11	*c*	1.1, 1.2 (2 t, 6), 3.53, 3.77 (2 q, 4), 7.2 (m, 14)
12	*b*	1.15 (t, 6), 3.3 (q, 4), 6.9 (m, 10)
14	*b*	1.18 (t, 3), 3.68 (q, 2), 7.2 (m, 9)
15	*b*	1.2 (t, 3), 1.87 (s, 3), 3.6 (q, 2), 7.0 (m, 9), 7.88 (s, 1)
16	*c*	1.13, 1.30 (2 t, 6), 3.51, 4.05 (m, 4), 6.45 (d, 2), 7.25 (m, 9), 8.0 (d, 2)
17	*b*	1.21, 1.25 (2 t, 6, J = 7), 3.13 (q, 2), 3.8 (s, 1), 4.08 (q, 2), 6.59 (d, 1, J = 8), 7.1 (m, 5), 7.82 (d, 1)
19	*c*	1.38 (t, 3), 4.23 (q, 2), 7.25 (m, 4), 7.93 (d, 1, J = 7.5), 8.19 (d of d, 1, J = 9, 2), 8.66 (d, 1, J = 2)
20	*c*	1.37 (t, 3), 2.17 (s, 3), 4.24 (q, 2), 7.40 (m, 8)
21	*c*	1.21, 1.33 (2 t, 6), 4.0, 4.21 (2 q, 4), 7.4 (m, 11)

[a] In δ units; J in hertz. [b] CCl_4. [c] $CDCl_3$. [d] Not found.

carbazole **17**, however, must be a secondary photoproduct, arising from **5b**. The formation of carbazoles by photocyclization of diphenylamines is well documented,[13] and we were able to convert **5b** into **17** by irradiation at 350 nm. The photodecomposition of **1b** has been reported by Child, *et al.*[14] Williams[15] has used the thermolysis of **1b** to study the reactions of *N*-ethylamino radicals. As far as we are aware, a quantitative report of the photoproducts of **1b** has not been given before.

Spin Trapping. The trapping of N-centered radicals as spin adducts is a fickle technique. Very few examples of successful trapping are known. The phthalimido radical has been trapped by methylene *tert*-butyl nitrone in the photolysis of azophthalimide.[16] The carbazolyl[17a] and the piperidinyl, azacyclononyl, and succinimidyl radicals[17b] have been trapped with 2-methyl-2-nitrosopropane, and the *N*-methylanilino radical with *3,5-d*$_2$-nitrosobenzene[18] in oxidation of carbazole and *N*-methylaniline with nickel peroxide. Attempts to trap the *N*-methylanilino radical from photolysis of **1a** with phenyl *tert*-butyl nitrone and with 3,5-di-*tert*-butyl-4-hydroxyphenyl *tert*-butyl nitrone failed, the former giving uninterpretable esr spectra and the latter undergoing hydrogen abstraction to give the phenoxyl radical.[19] It is thought[20] that phenyl *tert*-butyl nitrone is not particularly effective in trapping N-centered radicals.

We find that nitrosarenes are effective in trapping *N*-methyl- and *N*-ethylanilino radicals generated by photolysis of **1a** and **1b** (eq 3). Esr spectra of spin adducts **27–31**



27–31

a, R = Me; **b**, R = Et

Ar = C_6H_5 (**27**), C_6D_5 (**28**), *3,5-d*$_2$-C_6H_3 (**29**), 3,5-Cl_2-C_6H_3 (**30**), 3,5-(*t*-Bu)$_2$-C_6H_3 (**31**)

were recorded from trapping by nitrosobenzene (**22**) and perdeuterio- (**23**), 3,5-dideuterio- (**24**),[21] 3,5-dichloro- (**25**), and 3,5-di-*tert*-butylnitrosobenzene (**26**). Esr data are given in Table II. Spectra of spin adducts **27a**, **27b**, and **31a** are given as examples in Figures 1–3. The spectra have unresolved lines, and therefore small coupling constants were determined by simulating the spectra. Examples of simulation are given in Figures 1–3.

These results leave no doubt that *N*-alkylanilino radicals are formed under our conditions of irradiation of tetrazenes **1**. Unfortunately, we do not know if they may also recombine to products **3** and **5**. The failure that not only we but also others have met[11] in searching for photo-CIDNP effects with **1b** is impressive and suggests that **3b** is formed by radical recombination. We feel, though, that these negative results may not be reliably diagnostic and we regard them with caution until similar search can be made with other, suitably designed tetrazenes.

Experimental Section

1,4-Diethyl-1,4-diphenyl-2-tetrazene (1b). Mercuric oxide (42.2 g, 194 mmol) was added in portions to a cold solution of 12.7

Table II
Esr Data for the Spin Adducts (27–31) from the Photodecomposition of 1,4-Dimethyl- (1a) and 1,4-Diethyl-1,4-diphenyl-2-tetrazene (1b). Trapping of *N*-Methylanilino and *N*-Ethylanilino Radicals with Nitrosoarenes[a]

Tetrazene	ArNO	Adduct	g	$a_{\alpha\text{-N}}$	$a_{\beta\text{-N}}$	$a_{o,p\text{-H}}$	$a_{m\text{-H}}$
1a	**22**	**27a**	2.0055	12.19	0.57	2.93	0.96
1a	**23**	**28a**	2.0055	11.97	*b*	*b*	*b*
1a[c]	**23**	**28a**	2.0055	11.58	*b*	*b*	*b*
1a	**24**	**29a**	2.0055	11.91	0.59	2.78	
d	**24**	**29a**	2.0052	12.05	0.63	2.83	
1a	**25**	**30a**	2.0054	11.29	*b*	2.76	
1a	**26**	**31a**	2.0054	12.10	0.59	2.82	
1b[e]	**22**	**27b**	2.0055	11.80		2.83	0.96
1b	**22**	**27b**	2.0055	11.94		2.86	0.94
1b	**23**	**28b**	2.0055	11.86	*b*	*b*	*b*
1b	**24**	**29b**	2.0054	11.80	*b*	2.76	
1b	**25**	**30b**	2.0054	10.98	*b*	2.75	
1b	**26**	**31b**	2.0054	12.03	0.59	2.83	

[a] See eq 3. All solutions were in benzene at approximately 25° unless otherwise stated. [b] Unresolved. [c] In *n*-hexane at −34°. [d] Terabe and Konaka[18] by oxidation of *N*-methylaniline. [e] In cyclohexane.

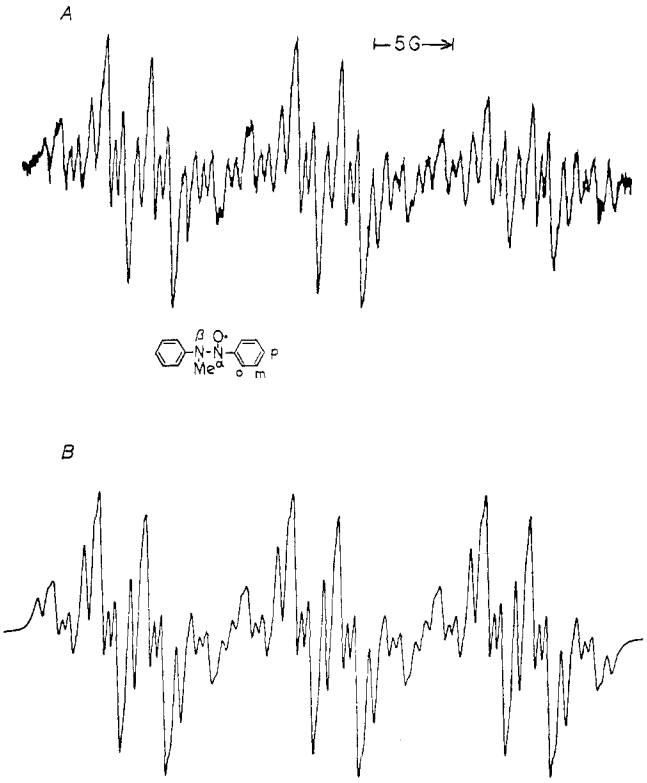


Figure 1. Experimental (A) and simulated (B) esr spectra of the spin adduct (**27a**) of *N*-methylanilino radical, from irradiation of **1a**, and nitrosobenzene in benzene solution.

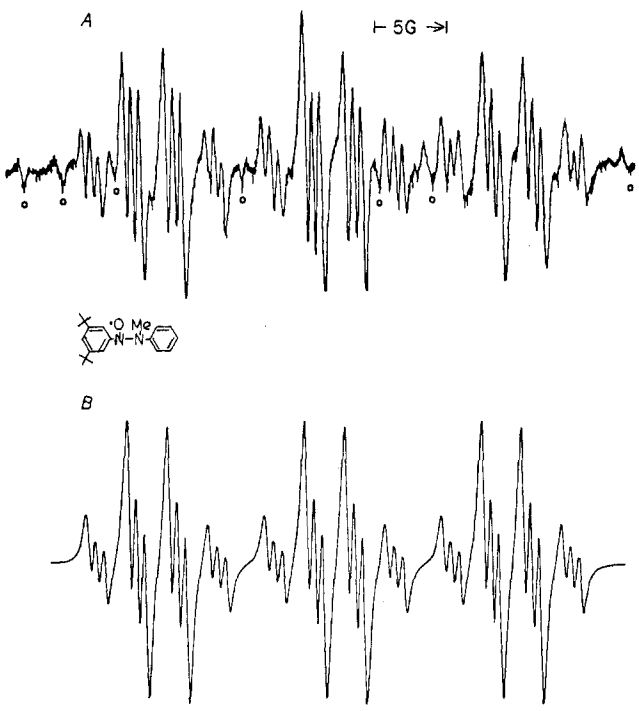


Figure 2. Experimental (A) and simulated (B) esr spectra of the spin adduct (**31a**) of *N*-methylanilino radical, from irradiation of **1a**, and 3,5-di-*tert*-butylnitrosobenzene in benzene solution. Lines of an unidentified signal in A are marked with an open circle.

g (93.4 mmol) of 1-ethyl-1-phenylhydrazine (**2b**)[22] in dry ether. After stirring in an ice bath for 2.5 hr the mixture was worked up to give 4.0 g of **1b**, mp 114–115° dec (ether–ethanol), with acceptable nmr spectrum (lit. mp 113°).[15]

1,4-Dimethyl-1,4-diphenyl-2-tetrazene (1a) was prepared similarly from 1-methyl-1-phenylhydrazine (**2a**) and had mp 140.5–141° (lit.[23] mp 141–142°).

***N,N'*-Diethylhydrazobenzene (3b).** A solution of 4.5 g (24

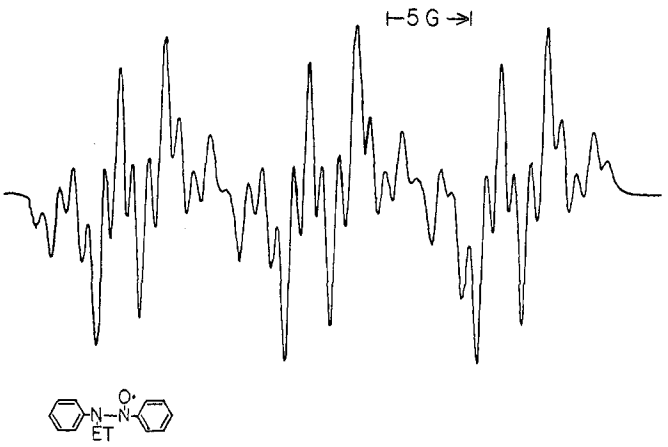


Figure 3. Esr spectrum of the spin adduct (**27b**) of *N*-ethylanilino radical, from irradiation of **1b**, and nitrosobenzene in benzene solution.

mmol) of hydrazobenzene in 160 ml of THF was cooled in ice and kept flushed with N_2 gas. To this was added 11 ml of commercial 90% *n*-butyllithium solution. When gas evolution had stopped, 17 ml of ethyl bromide was added to the orange-red solution, and the solution was stirred for 3 hr. Ether (50 ml) was added and the mixture was washed with water and worked up to give 6.4 g of yellow oil, which was chromatographed with petroleum ether (bp 30–60°) on a neutral alumina column to give 5.3 g (90%) of oil. The oil was crystallized from ethanol–ether at low temperature, but could not be kept as a solid. **3b**, mp 40–40.5°, has been prepared[24] by reaction of ethyl bromide–pyridine with hydrazobenzene.

Anal. Calcd for $C_{16}H_{20}N_2$: C, 79.9; H, 8.39; N, 11.7. Found: C, 80.1; H, 8.69; N, 12.0.

***N*-Ethylaniline (4b)** was prepared by reducing acetanilide with lithium aluminum hydride in THF. The product was distilled in 81% yield under reduced pressure, and gave a *p*-toluenesulfonyl derivative, mp 87–87.5° (lit.[25] mp 87°).

***N,N'*-Diethyl-*N*-phenyl-*p*-phenylenediamine (*N,N'*-Diethyl-*p*-semidine) (5b).** Commercial (Eastman Kodak, technical grade) *N*-phenyl-*p*-phenylenediamine (9.1 g, 50 mmol) was acetylated with 5 ml of acetyl chloride in 30 ml of pyridine. The solution was extracted with $CHCl_3$ after pouring onto dilute hydrochloric acid, to give 7.5 g (66%) of 4-acetamidodiphenylamine (**7**), mp 160–161° (lit.[26] mp 158°).

7 was ethylated in THF and in DMF solution. A suspension of 6.73 g (29.8 mmol) of **7** and 3.0 g (71 mmol) of NaH (from commercial suspension in mineral oil after washing with petroleum ether) in dry THF was boiled for 70 min. After cooling, an excess of ethyl bromide was added dropwise, and the solution was stirred at room temperature for 3 hr. Work-up and extraction with ether gave 8.3 g of brown oil. Trituration with CCl_4 gave 2.7 g of recovered **7**, mp 162–163°. The residue was chromatographed on a silica gel column. The first eluate, 500 ml of benzene, was discarded. Next, 500 ml of benzene–ether (80:20) gave 1.45 g (16%) of *N,N'*-diethyl-4-acetamidodiphenylamine (**8**) as an oil. The nmr spectrum agreed with structure **8**. Attempted crystallization failed.

Continued elution with benzene–ether (60:40, 500 ml) gave 1.8 g of an oil which was triturated with ether–petroleum ether to give 0.21 g (2.8%) of 4-(*N*-ethylacetamido)diphenylamine (**10**), mp 159.5–160° (ether), with acceptable nmr spectrum.

Anal. Calcd for $C_{16}H_{18}N_2O$: C, 75,6; H, 7.13; N, 11.0. Found: C, 75.5; H, 7.36; N, 11.2.

Concentration of the ether–petroleum ether solution (above) gave 0.26 g (3.4%) of 4-acetamido-*N*-ethyldiphenylamine (**9**), mp 113.5–114.5°, with acceptable nmr spectrum.

For ethylation of **7** in DMF a suspension of 6.73 g (29.8 mmol) of **7** and 3.3 g (78 mmol) of NaH in 50 ml of DMF was used. This was kept at 105° for 2 hr before ethylation with 15 ml of ethyl bromide. Work-up as above gave, from 1 l. of benzene–ether (85:15), 2.5 g (29%) of **8**, with acceptable nmr spectrum, and 0.36 g (4.7%) of **10**, mp 154–156°.

The crude compound **8** from the DMF reaction was boiled for 14 hr with 10 g of KOH in 20 ml of 50% aqueous ethanol. Work-up gave 1.8 g of red oil. This was chromatographed on alumina with petroleum ether–ether (90:10) to give 1.05 g (49%) of the

N,N'-diethyl-*p*-semidine (**5b**), mp 49–49.5° (petroleum ether), with acceptable nmr spectrum.

Anal. Calcd for $C_{16}H_{20}N_2$: C, 79.96; H, 8.39; N, 11.7. Found: C, 80.0; H, 8.37; N, 11.5.

The benzenesulfonyl derivative (**11**) had mp 76–77° (ethanol) and acceptable nmr spectrum.

***N,N*-Diethyl-*N'*-phenyl-*p*-phenylenediamine (12).** A solution of 0.36 g (1.42 mmol) of 4-(*N*-ethylacetamido)diphenylamine (**10**) from the above ethylations and 0.8 g (21 mmol) of lithium aluminum hydride in 15 ml of THF was boiled for 13 hr. Work-up gave 0.36 g of yellow oil which was chromatographed on neutral alumina. The first 100 ml of petroleum ether–ether (90:10) was discarded. Next, 200 ml (80:20) gave 0.28 g (82%) of *N,N*-diethyl-*N'*-phenyl-*p*-phenylenediamine (**12**), mp 88.5–89.5° (petroleum ether), with acceptable nmr spectrum (lit.[27] mp 87°).

***N,N'*-Diethyl-*N*-phenyl-*o*-phenylenediamine (*N,N'*-Diethyl-*o*-semidine) (6b).** *N*-Ethyl-2-nitrodiphenylamine (**14**), mp 49–50°, was prepared from 2-nitrodiphenylamine (**13**) by the method of Storrie and Tucker (lit.[28] mp 50–51°). **14** was reduced and acetylated to give 2-acetamido-*N*-ethyldiphenylamine (**15**) as an oil, as found also by the earlier workers.[28] Both **14** and **15** had acceptable nmr spectra.

Reduction of **15** (1.6 g, 6.3 mmol) was achieved by boiling with 2.0 g of lithium aluminum hydride in 75 ml of ether for 12 hr. Work-up gave 1.52 g of an oil which was distilled under reduced pressure to give 1.19 g (79%) of the *N,N'*-diethyl-*o*-semidine (**6b**), with acceptable nmr spectrum. The *p*-nitrobenzoyl derivative (**16**) had mp 159–160° (ethanol).

Anal. Calcd for $C_{23}H_{23}N_3O_3$: C, 70.93; H, 5.92; N, 10.8. Found: C, 70.94; H, 6.13; N, 10.50.

3-(*N*-Ethylamino)-9-ethylcarbazole (17). 3-Nitrocarbazole (**18**) was prepared by nitration of carbazole;[29] the crude product had mp 197–201° (lit. mp 214°,[29] 205°[30]). Compound **18** was ethylated with diethyl sulfate in aqueous acetone–KOH solution. The crude product was purified by chromatography several times on alumina and gave from petroleum ether–ether (60:40) 2.6 g of *N*-ethyl-3-nitrocarbazole (**19**), mp 129.5–130° (ether), 65% (lit.[31] mp 126–128°).

19 was reduced and acetylated as follows. A mixture of 3.0 g (12.5 mmol) of **19**, 3 g of sodium acetate, and 3.7 ml of acetic anhydride in 150 ml of ethyl acetate was stirred with 0.31 g of Pd/C catalyst under H_2 at 1 atm for 23 hr. Filtering and evaporation of solvent gave 3.6 g of solid. Trituration with ether gave 1.8 g (31%) of 3-acetamido-*N*-ethylcarbazole (**20**), mp 198–199° (benzene–ethanol), with acceptable nmr spectrum (lit.[32] mp 203–204°).

20 was reduced with lithium aluminum hydride as follows. A suspension of 2.4 g of **20** and 1 g of lithium aluminum hydride in 25 ml of THF was boiled for 6 hr. Work-up gave 2.0 g of an oil which was chromatographed on neutral alumina giving, from 2 l. of petroleum ether–ether (90:10), 1.8 g of a red oil. This was rechromatographed on silica gel. First, 1300 ml of eluent (90:10) was discarded. Next, 1 l. (80:20) gave 1.6 g of yellow oil which was distilled at 167–169° (1 mm) to give 0.9 g (41%) of an oil which solidified in the refrigerator. Crystallization gave 3-(*N*-ethylamino)-9-ethylcarbazole (**17**), mp 72.5–73° (*n*-hexane–ether), with acceptable nmr spectrum. The *p*-nitrobenzoyl derivative (**21**) had mp 180.5–181° (ether).

Anal. Calcd for $C_{23}H_{21}N_3O_3$: C, 71.3: H, 5.46; N, 10.8. Found: C, 71.4; H, 5.68; N, 10.6.

Irradiation of 1,4-Diethyl-1,4-diphenyl-2-tetrazene (1b). A solution of 500 mg (1.86 mmol) of **1b** in 160 ml of cyclohexane (Eastman, Spectrograde) was degassed and sealed in a Pyrex tube and irradiated at 350 nm for 135 min in a Rayonet photochemical reactor at 18°. The solvent was removed under vacuum, leaving 486 mg of yellow oil, which was chromatographed on neutral alumina (Woelm III). Petroleum ether (1 l.) gave 209 mg (47%) of **3b**, identified by comparison with an authentic sample. Petroleum ether–ether (98:2, 500 ml) gave 90 mg (20%) of **4b**; 500 ml (95:5) gave 6 mg of unidentified oil; 1 l. (90:10) gave 26 mg (6%) of **5b**, identified by comparing the tlc, ir, nmr, and benzenesulfonyl derivative with those of authentic **5b**; 300 ml (70:30) gave 26 mg (6%) of **17**, identified by comparing the tlc and nmr with those of authentic **17**, The *o*-semidine (**6b**) was not found.

A control sample of 500 mg of **1b** wrapped in aluminum foil was irradiated at the same time. Removal of solvent and trituration of the residue with ethanol left 473 mg (95%) of recovered **1b**. The ethanol filtrate showed only one spot by tlc, corresponding with **1b**.

Photocyclization of *N,N'*-Diethyl-*N*-phenyl-*p*-phenylenediamine (5b). A solution of 300 mg (1.25 mmol) of **5b** in 150 ml of cyclohexane was treated as above for 4 hr at 25°. Removal of the solvent gave 285 mg of yellow oil. Chromatography on neutral alumina gave 81 mg (21%) of recovered **5b** and 91 mg (30.5%) of **17**, identified by nmr and the *p*-nitrobenzoyl derivative (**21**), mp 179–181°. An unidentified oil (21 mg) was obtained by continued elution.

Nmr spectra were recorded on a Varian A-60A spectrometer. Patterns are listed in Table I.

Spin Traps. Nitrosobenzene (**22**) was obtained commercially. Perdeuterionitrosobenzene (**23**) was prepared from commercial perdeuterionitrobenzene. 3,5-Dideuterionitrosobenzene (**24**) was a gift from Dr. Ryusei Konaka. 3,5-Dichloronitrosobenzene (**25**) was prepared from 3,5-dichloronitrobenzene and was purified by steam distillation, mp 98–99° (ether).[33] 3,5-Di-*tert*-butylnitrosobenzene (**26**) was prepared by oxidation of 3,5-di-*tert*-butylaniline[34] with *m*-chloroperbenzoic acid,[35] and had mp 93–94° (ethanol) (lit.[36] mp 93–95°).

Spin Trapping. Solutions were 5×10^{-2} *M* in tetrazene and $5\text{–}9 \times 10^{-2}$ *M* in spin trap, and were degassed by four freeze–thaw cycles. The silica esr tube was sealed and irradiated in the esr cavity at room temperature. A PEK 100-W mercury lamp was used with an adjustable focusing system. The light beam was filtered through a piece of 2-mm window glass to minimize decomposition of the spin trap. A dual-sample cavity was used with Fremy's salt as the standard. Steady-state concentrations of the spin adducts could be maintained only by continuous irradiation.

Simulation of successful spin-trapping spectra was carried out at the University of Texas.[37] Esr data are given in Table II.

Some spin traps failed to give spin-trapping spectra or gave spectra that did not appear to be attributable to spin-trapping radicals from the tetrazenes. These were 2-methyl-2-nitrosopropane, which decomposed in ether under irradiation conditions, methylene *tert*-butyl nitrone, and methylene-d_2 *tert*-butyl nitrone, which gave unidentified spin adducts (in both benzene and cyclohexane).

CIDNP Experiments. Solutions of **1b** were irradiated in the probe of an nmr instrument. In our own laboratory incident light was conveyed to the nmr tube along a quartz rod insert. In the Kyoto and Bell Telephone Laboratories, irradiation into the probe was direct. The solvents used were $CDCl_3$, CCl_4, and cyclohexane. In no case were CIDNP signals detected. In particular, repeated attempts were made at Bell Telephone using argon-purged cyclohexane without observing a single promising CIDNP line.

Registry No.—**1a,** 5579-27-1; **1b,** 40756-80-7; **2a,** 618-40-6; **2b,** 644-21-3; **3b,** 43199-88-8; **4b,** 103-69-5; **5b,** 43199-89-9; **6b,** 43199-90-2; **7,** 38674-90-7; **8,** 43199-92-4; **9,** 43199-93-5; **10,** 43199-94-6; **11,** 43199-95-7; **12,** 43199-96-8; **14,** 43199-97-9; **15,** 43199-98-0; **16,** 43199-99-1; **17,** 43200-00-6; **18,** 3077-85-8; **19,** 86-20-4; **20,** 6954-68-3; **21,** 43200-04-0; **27a,** 43200-05-1; **27b,** 43200-06-2; **28a,** 43200-07-3; **28b,** 49564-69-4; **29a,** 39520-59-7; **29b,** 43200-09-5; **30a,** 43200-10-8; **30b,** 43200-11-9; **31a,** 43200-12-0; **31b,** 43200-13-1.

References and Notes

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(12) The term initial is used instead of primary to avoid mechanistic implications with the term primary. The latter implies that **5a** and **5b** are formed only by a concerted process, and not by radical recombination. We are unable to make a clear decision on this point.
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(21) We thank Dr. Konaka for the gift of a sample of **24**.
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The Reaction of Methanesulfonyl Nitrene with Benzene. Attempts to Generate Sulfonyl Nitrenes from Sources Other than the Azides

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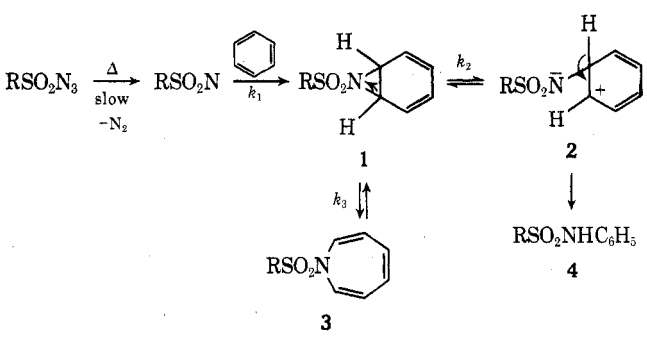
The reaction of methanesulfonyl nitrenes with benzene and other aromatic compounds has been studied in detail. The results have been rationalized in terms of the addition of the singlet nitrene to the aromatic molecule to give a benzaziridine intermediate which, under kinetic control conditions, gives the *N*-mesylazepine and, under conditions of thermodynamic control, gives the *N*-mesylanilines. While the azepines could not be detected in the thermolysis at 120° they could be trapped with tetracyanoethylene. At lower temperatures the *N*-mesylazepine itself could be isolated. Numerous attempts have been made at generating singlet sulfonyl nitrenes under mild conditions either by photolysis of sulfonyl azides or from nonazide precursors. No encouraging results were obtained.

Thermal decomposition of sulfonyl azides in aromatic solvents occurs slowly at 120°. The decomposition is unimolecular,[1] leading to a singlet nitrene.[2] This is followed by an addition to the aromatic nucleus to give a benzaziridine intermediate (**1**), with ring opening of the latter to form the observed *N*-sulfonamides[2] being a relatively fast, thermodynamically controlled process. The unsubstituted primary sulfonamides, products of hydrogen abstraction by the nitrene, are also formed in these reactions. In contrast to the reactions with ethyl azidoformate[3] and with cyanogen azide,[4] no sulfonylazepine (**3**) could be detected, even by thin layer chromatography which was shown, in control experiments, to permit detection of *ca.* 0.1% of **3**.



In an attempt to trap the benzaziridine **1**, the reaction between methanesulfonyl azide and benzene was repeated at 120° in the presence of tetracyanoethylene (TCNE).[5,6] A crystalline 1:1 adduct, $C_{13}H_9N_5O_2S$, was obtained (29.4%) and was formed at the expense of **4**, whose yield dropped from 54 to 6%. Methanesulfonamide (19%, up from 14%) was also obtained. The nmr spectrum of the adduct indicated clearly that it was not the symmetrical product **5** that would have resulted from a $[\pi 2_s + \pi 4_s]$ addition of TCNE to **1**. Indeed, spin-decoupling experiments confirmed that it had the partial structure **6**, and hence that it was the 1,4 adduct (**7**) of TCNE and *N*-methanesulfonylazepine (**3**). Thus, H_A gave rise to an octet (J_{AC} = 8.6, J_{AF} = 7.3, J_{AD} = 1.0 Hz) at δ 7.01, H_B gave rise to another octet (J_{BE} = 8.6, J_{BD} = 1.5, J_{BF} = 0.5 Hz) at δ 6.67, H_C gave rise to an octet (J_{CD} = 7.0, J_{AC} = 8.6, J_{CF} = 1.0 Hz) at δ 6.6, and H_D also gave rise to an octet (J_{CD} = 7.0, J_{AD} = 1.0, J_{BD} = 1.5 Hz) at δ 5.68, while H_E gave a triplet (J_{EF} = J_{BE} = 8.6 Hz) at δ 5.28, H_F gave a complex multiplet (J_{AF} = 7.3, J_{EF} = 8.6, J_{CF} = 1.0, J_{BF} = 0.5 Hz) at δ 3.91, and H_{Me} gave rise to a singlet at δ 3.32. These assignments are similar to those made by Kende and his coworkers[7] for the corresponding adduct between TCNE and *N*-ethoxycarbonylazepine. The structure of the adduct was confirmed by synthesizing an authentic sample from *N*-mesylazepine (kindly supplied by Dr. L. A. Paquette) and TCNE; the product was identical with that trapped in the azide thermolysis.

Similar adducts were obtained from the decomposition of methanesulfonyl azide in toluene and in chlorobenzene. In these cases, it is clear that a number of monosubstituted azepines can arise and that each one, in turn, may give one or more Diels–Alder products with TCNE. The nmr of the adduct from the toluene reaction suggests that it consists of a single isomer, namely **8**. It was very similar to that of **7**. Thus H_A gives rise to a quartet (J_{AB} = 8.6, J_{AE}