# Photolysis of Unsymmetric Azo Compounds. Cis Azo Compound Intermediates[1]

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**Abstract:** Syntheses of unsymmetric aryl–alkyl azo compounds *via* oxidation of unsymmetric sulfamides or ureas are reported. The azo compound *N*-phenyl-*N'*-(2-phenyl-2-propyl)diazene (**6**) decomposes photochemically in benzene to give dicumyl and biphenyl as the major products. Optically active *N*-phenyl-*N'*-(2-phenyl-2-butyl)-diazene (**1**) photoracemizes as well as photodecomposes. Low-temperature photolysis of **6** leads only to trans–cis photoisomerization with little or no decomposition. The cis azo compound thus formed is stable at temperatures up to 0° but it decomposes in benzene at room temperature to give the trans isomer along with dicumyl and biphenyl. Photolysis of **6** at 15° leads to a rapid buildup of *cis*-**6** followed by a slow increase in photodecomposition products. Optically active *cis*-**1** is produced by low-temperature photoequilibration with *trans*-**1**. The photoequilibration occurs without any attending racemization (at −78°). Optically active *cis*-**1** decomposes at 25° to give the trans isomer which is partially racemized. These results are interpreted as meaning that unsymmetric aryl–alkyl azo compounds photodecompose by isomerization followed by a one-bond scission decomposition of the unstable cis isomer.

Although azo compounds have been used as a source of free radicals for over 40 years, the mechanism of their decomposition is still a question of considerable debate. Early kinetic studies of azo thermal decomposition[2] led to the conclusion that the rate-determining step involves simultaneous rupture of both nitrogen–carbon bonds.

$$\underset{\text{two-bond scission}}{R{-}N{=}N{-}R \longrightarrow R\cdot \quad N_2 \quad \cdot R} \qquad (1)$$

The classic studies of Seltzer,[3] however, suggested that at least for unsymmetrically substituted azo compounds, one-bond rupture occurs.

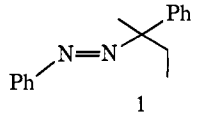
$$\underset{\text{one-bond scission}}{R{-}N{=}N{-}R' \rightleftharpoons R{-}N{=}N\cdot \cdot R' \longrightarrow R\cdot \quad N{\equiv}N \cdot R'} \qquad (2)$$

Pryor and Smith[4] also concluded that phenylazotriphenylmethane decomposes thermally by the one bond scission pathway. In addition, Pryor[4] notes that recombination of the initially formed radical pair (internal return) competes with diffusion of the radicals from the solvent cage, thus requiring the lifetime of the phenyldiazenyl radical to be on the order of the cage lifetime, if not longer. Neuman, Lockyer, and Amrich[5] supported the one-bond scission, internal return mechanism by measuring the activation volumes for decomposition of phenylazotriphenylmethane. The large activation volume they found is consistent with the internal return hypothesis put forward by Pryor.

More recently, Crawford[6] has proposed that not only unsymmetric but also some symmetric azo compounds decompose in the gas phase by the one bond scission pathway.

Although azo compounds were known to decompose photochemically as well as thermally, the problem of the mechanism of azo photodecomposition was not attacked with the same vigor as the thermolysis problem until the last 3–4 years. Mill and Stringham[7] pointed out that alkyl azo compounds trans–cis photoisomerize as do the azobenzenes.[8] However, the cis alkyl azo compounds thus formed are thermally unstable, even at −20°. Earlier, Hutton and Steel[9] had recognized the importance of trans–cis photoisomerization for azomethane and azoisopropane.

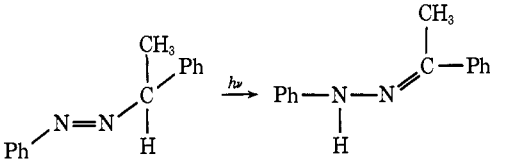
We sought to use stereochemistry as a tool for answering the question of "one-bond" or "two-bond" scission (thermal and photochemical).[10] With this goal in mind, syntheses of a number of unsymmetric aryl–*tert*-alkyl azo compounds were developed. Optically active **1** was initially our target molecule since we



**1**

intended to use the asymmetric center $\alpha$ to the azo linkage as a probe for studying its photochemistry.

Mechanistic photostudies of azo compounds are plagued by a complicating isomerization side reaction if the carbon $\alpha$ to the azo linkage is substituted by hydrogen. Thus the azo compound **2** photoisomerizes to **3** upon irradiation. **1** has the structural advantage



**2** **3**

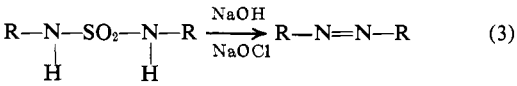
that photoisomerization to the phenylhydrazone cannot occur since there is no hydrogen on the $\alpha$ carbon.

(1) Supported by a grant from the National Science Foundation (GP27650).
(2) H. C. Ramsperger, *J. Amer. Chem. Soc.*, **51**, 2134 (1929).
(3) S. Seltzer and F. T. Dunne, *ibid.*, **87**, 2628 (1965).
(4) W. A. Pryor and K. Smith, *ibid.*, **92**, 5403 (1970).
(5) R. C. Neuman, Jr., G. D. Lockyer, Jr., and M. J. Amrich, *Tetrahedron Lett.*, 1221 (1972).
(6) K. Tagaki and R. J. Crawford, *J. Amer. Chem. Soc.*, **93**, 5910 (1971); **94**, 7406 (1972).
(7) T. Mill and R. S. Stringham, *Tetrahedron Lett.*, 1853 (1969).
(8) For a review, see D. L. Ross and J. Blanc, "Photochromism," G. H. Brown, Ed., Wiley, New York, N. Y., 1971, p 500.
(9) R. F. Hutton and C. Steel, *J. Amer. Chem. Soc.*, **86**, 745 (1964).
(10) Recent studies of the stereochemical course of unsymmetric azo compound thermolysis have appeared: A. Tsolis, S. Mylonakis, M. Nieh, and S. Seltzer, *ibid.*, **94**, 829 (1972); R. A. Johnson and S. Seltzer, *ibid.*, **95**, 938 (1973).

We report here the synthesis and study of **1** and other related azo compounds.

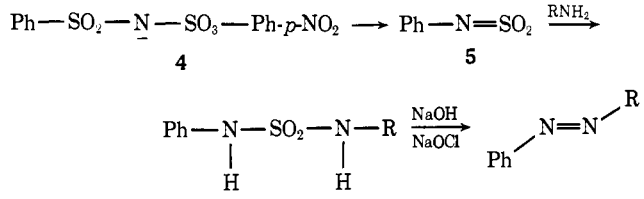
## Results

**Synthesis of Aryl-*tert*-Alkyl Azo Compounds.** The hypochlorite oxidation of symmetric sulfamides developed by Ohme and Schmitz[11] is a convenient method for the synthesis of symmetric azo compounds.[12]



(3)

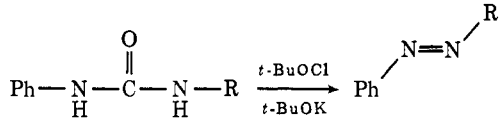
The unsymmetric aryl-*tert*-alkyl azo compounds were synthesized by essentially the same procedure, oxidation of unsymmetric sulfamides with sodium hydroxide and sodium hypochlorite. The previously unknown sulfamides were prepared by trapping sulfurylaniline (**5**) with primary amines. Sulfurylaniline was generated *in situ via* a Lossen-type rearrangement of the triethylammonium salt of *N*-(*p*-nitrobenzenesulfonoxybenzene)sulfonamide (**4**).[13] By decomposing the salt **4**, in the presence of a threefold



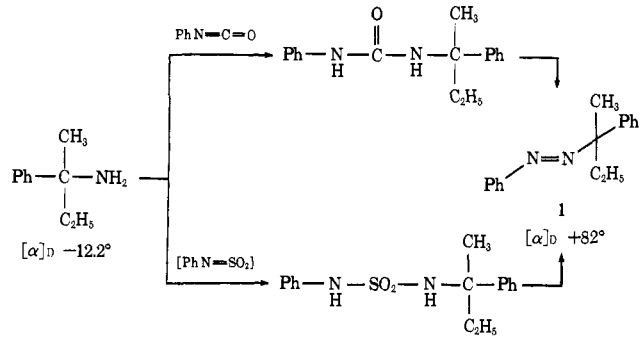
excess of amine, the desired sulfamide could be obtained in 65–75% yield.

Sulfurylaniline could be trapped by a variety of amines in this way to yield the unsymmetric sulfamide in good yield. The final step of the synthesis, oxidation by hypochlorite, proceeded in low yield, however (20–30%).

Recently, Fowler[14] has reported a much more convenient method for synthesis of the unsymmetric azo compounds. This superior method, which we used in the latter stages of our work, involves conversion of the readily available unsymmetric urea to the azo compound by the use of *tert*-butyl hypochlorite and *tert*-butoxide.

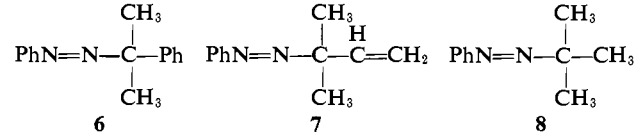


The advantage of both the sulfamide and urea synthetic routes is that *tert*-alkyl primary amines which have been resolved by standard techniques may be employed. Thus, optically active aryl-alkyl azo compounds, such as **1**, are readily available. For example, 2-phenyl-2-butylamine which had been previously resolved with l-malic acid[15] could be converted *via* either the sulfamide or urea to the optically active azo compound. **1** had a n–$\pi^*$ uv absorption at 416 nm



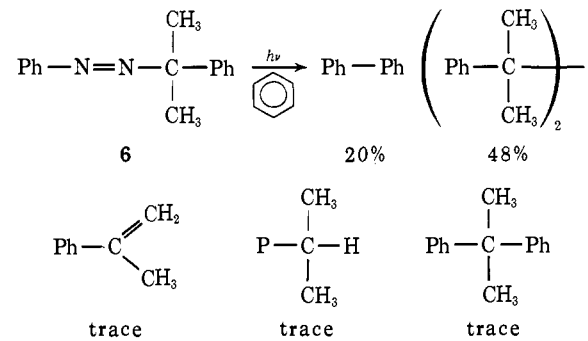
($\epsilon$ 121) and also had a strong CD absorption ($\Delta\epsilon_{max}$ +0.34, 416 nm).

Several other azo compounds such as **6–8** were



synthesized by the unsymmetric urea oxidation method.

**Photochemistry. Products.** A product study of the photodecomposition (medium-pressure Hg light, Pyrex filter) of **6** in benzene showed dicumyl and biphenyl to be the major products of decomposition. $\alpha$-Methylstyrene, 2,2-diphenylpropane, and cumene were formed in trace amounts. Unidentified nonvolatile products were also formed (probably quaterphenyls, etc., from radical attack on the solvent). Photodecomposition of **6** in cumene led to dicumyl as



the major product (65%) with benzene also formed in 64.5% yield.

The most striking feature of the photochemical decomposition of optically active **1** is that racemization of the azo compound accompanies photodecomposition. Thus, optically active **1** which is photodecomposed to 40% completion is recovered and found to retain only about 74% of the activity of the starting azo compound. In addition, the quantum yield for decomposition, as previously reported, is solvent viscosity dependent.[16] Thus, in viscous solvents (hexadecane) the quantum yield is low (0.029) compared with the quantum yield found in less viscous solvents (pentane, 0.051). These data were previously interpreted[16] by requiring a phenyldiazenyl radical intermediate which either undergoes internal return to give partially racemized azo compound or diffuses into solution where ultimately nitrogen and the phenyl radical are produced.

(11) R. Ohme and E. Schmitz, *Angew. Chem., Int. Ed. Engl.*, 4, 433 1965).

(12) (a) F. D. Greene, M. A. Berwick, and J. C. Stowell, *J. Amer. Chem. Soc.*, 92, 867 (1970); (b) J. C. Stowell, *J. Org. Chem.*, 32, 2360 (1967).

(13) W. Lwowski and E. Schieffle, *J. Amer. Chem. Soc.*, 87, 4359 (1965).

(14) J. S. Fowler, *J. Org. Chem.*, 37, 510 (1972).

(15) D J. Severn and E M. Kosower, *J. Amer. Chem. Soc.*, 91, 1710 (1969).

(16) N. A. Porter, M. E. Landis and L J. Marnett, *ibid.*, 93, 795 (1971).

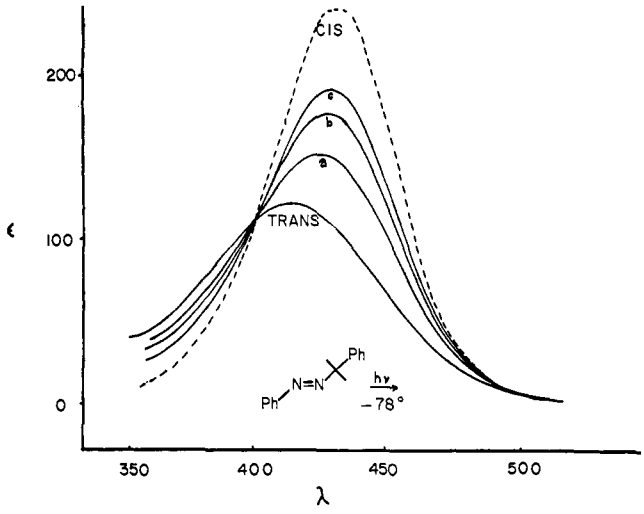



Figure 1. Uv spectra obtained during −78° photolysis of *trans*-**6** with 366-nm light: (a) after 0.5 hr, (b) after 1 hr, (c) after 2 hr.

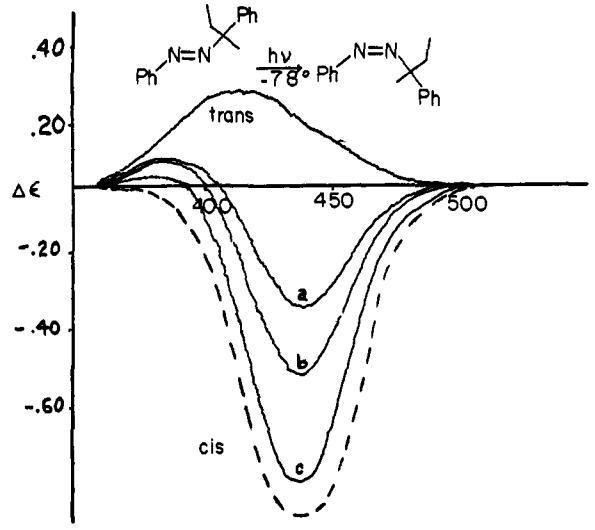
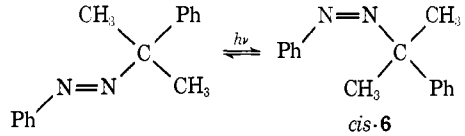



Figure 2. CD spectra obtained during −78° photolysis of *trans*-**1** with 366-nm light: (a) after 0.5 hr, (b) after 1 hr, (c) after 2 hr.

A recent CIDNP study[17] confirmed the intermediacy of the phenyldiazenyl radical and pointed to the possible importance of cis azo compounds as key intermediates in the photolysis.

**Low-Temperature Photolysis.** To further elucidate the mechanism of the photodecomposition, low-temperature photochemical studies were carried out.

We observe that *trans*-**6** photoisomerizes rapidly at −40° (435 or 366 nm) with no concomitant decomposition. The low-temperature photolysis ($CDCl_3$ solvent) is monitored by nmr, and no new absorptions save those due to the cis isomer (6 H singlet $\delta$ 1.58, 10 H multiplet $\delta$ 6.5–8.0) are observed. In addition, during photolysis at −78° (pentane solvent) a steady shift of $\lambda_{max}$ to longer wavelength is observed along with an increase in the absorbance.




*trans*-**6** *cis*-**6**

The observation of an isosbestic point[18] at 395 nm during the photoisomerization also suggests that the only photoprocess occurring at −78° is trans–cis isomerization. In Figure 1 are presented the uv spectra observed during photolysis at −78° in pentane. The n–$\pi^*$ absorptions of cis alkyl azo compounds have been reported at longer wavelength than the trans isomer, and the molar absorptivity is generally higher for the cis than the trans isomer.

*cis*-**6** could be isolated by low-temperature chromatography and proved to be a remarkably stable solid. It is stable for several hours at room temperature in the crystalline form and decomposes with nitrogen evolution at 49°. The uv ($\lambda_{max}$ 435 nm ($\epsilon$ 273)), ir, and nmr spectra of purified *cis*-**6** are consistent with its structure.

Photoisomerization of optically active **1** at −78° could be monitored by following the changes in the CD spectrum during photolysis. In Figure 2 are presented the CD spectra obtained during photolysis (366 nm) of *trans*-(+)-**1** in pentane. It is of interest to note that the maximum of the CD curve for the cis azo compound is much larger than and opposite in sign from the $\Delta\epsilon$ of the trans isomer: CD, cis ($\Delta\epsilon_{max}$ −0.86, 435 nm), trans ($\Delta\epsilon_{max}$ +0.34, 415 nm).

The low-temperature photoisomerization of **1** or **6** appears to be a simple photoequilibration[19] analogous to those observed in azobenzenes.[20] Photolysis with 366-nm light (predominantly trans absorbing) shifts the equilibrium in the cis direction; 436-nm photolysis (predominantly cis absorbing) shifts the equilibrium toward the trans. No racemization attends the photoequilibration of (+)-**1**. Thus, *trans*-(+)-**1** ($\Delta\epsilon_{415}$ +0.34) was photoequilibrated with its cis isomer for several hours at −78°, *trans*-(+)-**1** was isolated from the equilibrium mixture by low-temperature chromatography, and this recovered trans compound was of undiminished optical purity. Optically active *cis*-**1** recovered from the same equilibrium mixture by low-temperature chromatography had a uv ($\lambda_{max}$ 435 ($\epsilon$ 279)) and CD ($\lambda_{max}$ 435 ($\Delta\epsilon$ −0.86)). The fact that the same photoequilibrium state can be approached from the cis isomer supports the contention that photolysis for several hours results in a true photoequilibrium.

The low-temperature photochemistry of **1** and **6** is thus quite different from the room-temperature photochemistry. At room temperature, photolysis leads to racemization and decomposition whereas at −78° trans photoequilibrates with cis with no evidence for radical formation or racemization of the azo compound. It should be noted that the low-temperature photoequilibration relates the optical rotation of *trans*-**1** with that of *cis*-**1**. *trans*-**1** ($\Delta\epsilon_{415}$ +0.34) has the same optical purity as *cis*-**1** ($\Delta\epsilon_{435}$ 0.86) since no racemization occurs during the photoequilibration or low-temperature isolation.[21]

(17) N. A. Porter, L. J. Marnett, C. H. Lochmüller, G. L. Closs, and M. Shobataki, *J. Amer. Chem. Soc.*, **94**, 3664 (1972).

(18) After photolysis for extended periods (>10 hr), it appears that some azo compound is decomposing even at −78° and the isosbestic point is thus only observed through the first 5–8 hr of photolysis.

(19) See, for example, R. O. Kan, "Organic Photochemistry," McGraw-Hill, New York, N. Y., 1966, pp 19–30.

(20) P. D. Wildes, J. C. Pacifici, G. Drick, and D. G. Whilten, *J. Amer. Chem. Soc.*, **93**, 2004 (1971), and references cited therein.

(21) Control experiments show that no racemization of either *trans*-**1** or *cis*-**1** occurs during low-temperature chromatography.

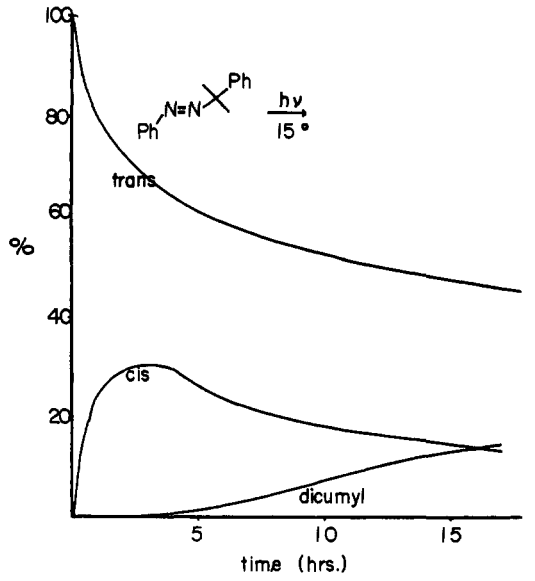


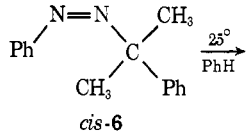

Figure 3. Photolysis product composition obtained during 15° photolysis of *trans*-**6** in $CDCl_3$ with a Pyrex filtered Hg medium-pressure lamp.

The fundamental importance of cis azo compounds as intermediates in the photodecomposition of the trans isomer is demonstrated by monitoring the photochemical decomposition of *trans*-**6** at 15° by nmr.[22] Figure 3 shows the results of this study. *Cis*-**6** is initially the only product formed.

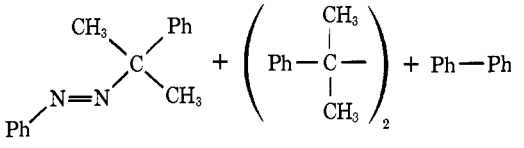
Other free radical decomposition products (dicumyl, the major product is shown as an example) build up later in the photolysis at the expense of the cis azo intermediate. This experiment rules out any significant amount of direct photochemical conversion of the trans azo compound to decomposition products at or near room temperature.

**Thermal Decomposition of Cis Azo Compounds.** *cis*-**1** and *cis*-**6** are thermally unstable in solution at room temperature and decompose to give free radical decomposition products as well as the trans isomers.

Thus, *cis*-**6** decomposes in benzene at 25° to give *trans*-**6**, dicumyl (13%), biphenyl, and other nonvolatile products. One striking feature of the decomposition of *cis*-**6** is that the amount of *trans*-**6**




*cis*-**6**




formed is dependent on the solvent viscosity. Table I shows the per cent conversion of cis to trans in four different straight chain hydrocarbon solvents.

The stereochemical course of the thermal decomposition of *cis*-**1** could be followed by isolating the product *trans*-**1** and determining its optical purity. In Table II the per cent retention of configuration of *trans*-**1** recovered from decomposition of *cis*-**1** in three straight chain hydrocarbon solvents is presented. Although there is not a great variation in the retention of configuration with the solvent, there does appear to be a general trend toward lower retention in the more viscous solvents. It seems worth noting that decomposition of *cis*-**1** in the presence of $BrCCl_3$, a good radical scavenger, does not significantly affect the per cent retention of configuration in *trans*-**1** formed. This experiment rules out any radical induced racemization of the azo compound.

(22) *cis*-**6** has a half-life of about 1 hr at 15°

**Table I.** Per Cent Yield of *trans*-**6** Formed in Thermolysis of *cis*-**6**

| % yield trans[a] | Solvent | % yield trans[a] | Solvent |
|---|---|---|---|
| 31.2 | Pentane | 45.3 | Decane |
| 37.0 | Octane | 49.8 | Dodecane |

[a] Amount trans formed analyzed by uv.

**Table II.** Per Cent Retention in Recovered *trans*-**1** Following Thermal Decomposition of *cis*-**1** at 25°

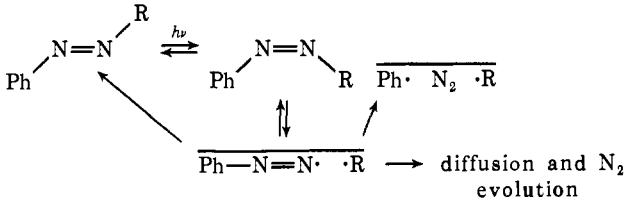
| Solvent | % retention in recovered trans |
|---|---|
| Pentane | 88.2 |
| Octane | 84.1 |
| Dodecane | 82.0 |

Both lines of investigation presented here support a "one-bond scission, internal return" mechanism for the thermal decomposition of the cis aryl–alkyl azo compounds studied. The variation in *trans*-**6** produced (Table I) is indicative of cage-type behavior[23] of the initially formed phenyldiazenyl–cumyl radical pair. The fact that racemization does occur during the conversion of *cis*-**1** to *trans*-**1** at 25° supports the contention that a nitrogen containing radical pair is an intermediate.

## Discussion

Several lines of evidence support the mechanism outlined in Scheme I for unsymmetric azo compound

**Scheme I**




photodecomposition. (a) Racemization of optically active **1** accompanies photodecomposition at room temperature.[16] (b) The quantum yield for decomposition of **1** is solvent viscosity dependent,[16] (c) CIDNP studies[17] support the intermediacy of a phenyldiazenyl–cumyl radical pair. The CIDNP studies also point to the possible involvement of cis azo compounds as key intermediates leading to the phenyldiazenyl radical. In support of the intermediacy of cis azo compounds, (d) Photolysis of **6** at 15° shows that hydrocarbon decomposition products follow a rapid buildup of the cis isomer. (e) Partially racemized *trans*-**1** is recovered

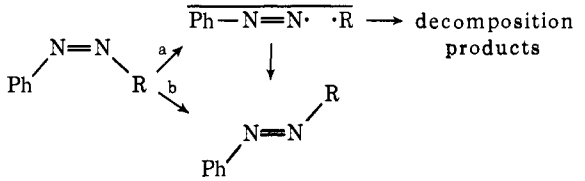
(23) For an excellent review, see E. M. Kosower, "Physical Organic Chemistry," Wiley, New York, N. Y., 1968.

in the thermal decomposition of *cis*-**1**. (f) The per cent yield of *trans*-**6** in the thermal decomposition of *cis*-**6** is solvent viscosity dependent. (g) The product distribution for photolysis of **6** is also consistent with the mechanism proposed in Scheme I. In particular, the low conversion of **6** to 2,2-diphenylpropane (the phenyl–cumyl radical pair coupling product) suggests that the phenyl–cumyl radical pair is not an important intermediate. We therefore conclude that $\beta$ scission of the phenyldiazenyl radical is slow compared to the diffusion of radicals from the solvent cage. Other workers have also noted that aryl–alkyl hydrocarbons are formed in low yield in aryl–alkyl azo decompositions.[24–26]

It seems likely that cis azo compounds are key intermediates in the photolysis of symmetric alkyl azo compounds as well as in the unsymmetric aryl–alkyl compounds reported here. Engel and Bartlett[27] and Mill and Stringham[7] suggest that the photoisomerization of azoisobutane is a key step in its photolysis. This suggestion is supported by the observation that the quantum yield for isomerization approaches the quantum yield for nitrogen evolution.[27]

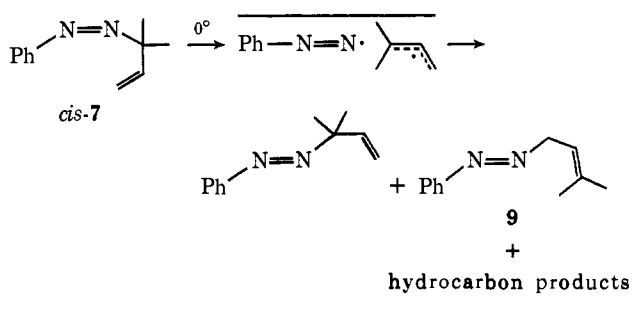
The tendency of *cis*-**1** and *cis*-**6** to decompose by one-bond scission to a radical pair contrasts with cis azobenzenes[28,29] where a nonradical isomerization to the more stable trans isomer occurs. Two possible reaction routes are thus available for cis azo compounds: (a) decomposition to radical pairs and (b) isomerization to the trans isomer without the intervention of radical species (Scheme II). The actual path

**Scheme II**




followed depends undoubtedly on the stability of the potential radical, ·**R**. For azobenzene (**R** = Ph), path b is preferred so that the formation of an unstable phenyl radical is avoided (path a). For **R** = cumyl, the radical path is now energetically feasible due to the stability of the cumyl radical.

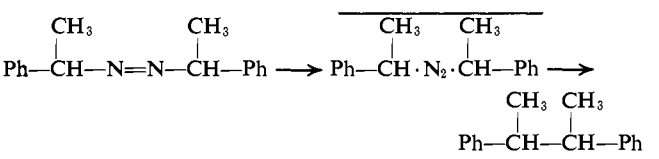
It should be noted that the cis isomer of **7** has also been prepared by low-temperature photolysis and chromatography of the trans isomer.




*cis*-**7** is much less stable than *cis*-**6**. This probably reflects the greater stability of the dimethallyl radical compared to the cumyl radical.[30]

*cis*-**7** decomposes in hydrocarbon solvents to give *trans*-**7** and the rearranged azo compound **9**. It would appear then, that *cis*-**7** plays a crucial role in the photochemistry of *trans*-**7**[31] analogous to the role played by the *cis*-arylcumyl azo compounds. That is, *cis*-**7** decomposes by path a giving the phenyldiazenyl–dimethylallyl radical pair.

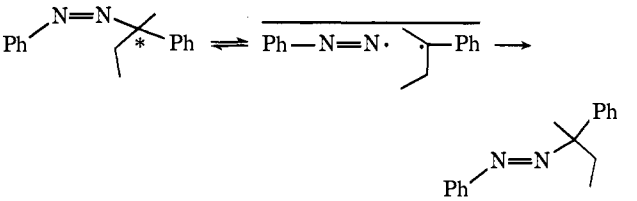
The stereochemical course of the decomposition of *cis*-**1** deserves comment. Greene and coworkers[12a] and Kopecky and Gillan[32] have investigated the stereochemical behavior of substituted azo compounds such as **10**. The high racemization observed in the




**10**

hydrocarbon products has been rationalized by the fact that nitrogen initially separates the radicals.[32] The intervening nitrogen effectively prolongs the pair lifetime and allows racemization to occur.

It is tempting to explain the rather high retention of configuration in the *cis*-**1** to *trans*-**1** conversion by arguing that nitrogen does not separate the initially formed radicals in this case so that high retention is expected. Following one-bond scission, no buffer molecule initially separates the radical centers. Therefore, internal return can occur rapidly before much racemization has occurred.




However, two facts suggest that caution must be exercised in interpreting the stereochemical conversion of *cis*-**1** to *trans*-**1**. (1) Internal return of the radical pair could occur to give either the cis or trans isomer.[33] Obviously, a significant amount of return to the cis isomer would complicate any arguments about the relative rates of radical racemization and recombination. (2) At this time, we cannot rule out the possibility that isomerization (Scheme II, path b) competes

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(25) H. Wieland, E. Popper, and H. Seefried, *Chem. Ber.*, **55**, 1816 (1922).
(26) D. H. Hey, *J. Chem. Soc.*, 1966 (1934).
(27) P. S. Engel and P. D. Bartlett, *J. Amer. Chem. Soc.*, **92**, 5883 (1970).
(28) G. Zimmerman, L. Y. Chow, and U. J. Park, *ibid.*, **80**, 3528 (1958).
(29) S. Ljunggren and G. Wettermark, *Acta Chem. Scand.*, **25**, 1599 (1971).
(30) (a) P. S. Engel and D. J. Bishop, *J. Amer. Chem. Soc.*, **94**, 1248 (1972); (b) P. S. Engel, personal communication. (c) Detailed kinetic studies of several cis azo compound decompositions have been carried out and appear elsewhere: N. A. Porter and M. O. Funk, *J. Chem. Soc., Chem. Commun.*, 263 (1973).
(31) (a) N A. Porter and P. M. Iloff, *Chem. Commun.*, 1575 (1971). (b) Recent esr work has been claimed to support the phenyldiazenyl radical as an intermediate [P. Stilbs, G. Ahlgren, and B. Akermark, *Tetrahedron Lett.*, 2387 (1972)]. We find, however, that esr signals observed during photolysis of **6** are better interpreted by postulating a minor side reaction involving radical addition to the azo compound giving a hydrazyl radical: L. J. Marnett, P. Smith, and N. A. Porter, *ibid.*, 1081 (1973).
(32) K. B. Kopecky and T. Gillan, *Can. J. Chem.*, 47, 2371 (1969).
(33) Professor G. Closs has informed us that CIDNP studies indicate that some return of the radical pair to the cis azo compound occurs.

to some extent with radical pair formation (path a). Cis–trans isomerization by path b would proceed with 100% retention of configuration. Therefore, any successful competition from this pathway would rule out interpretation of radical pair stereochemical behavior in this system.

It is of interest to note that little is known about the competition between paths a and b in Scheme II. In this regard, preliminary experiments indicate that *cis*-**8** follows only the isomerization pathway.[30c] No CIDNP signals are observed and *cis*-**8** proceeds to *trans*-**8** with no concomitant decomposition to nonazo products.

Conclusions about the relative rates of racemization and bond formation of the radical pair formed from *cis*-**1** would be speculative at this point due to the complications cited above. The higher racemization observed in viscous solvents (Table II) might be expected since the radicals are confined in their partners vicinity for a longer time and, as a consequence, more recombinations of racemized radicals result.

Further work is in progress to determine how structural variations affect the competition between radical pair formation and isomerization of cis azo compounds.

## Experimental Section

Melting points are reported uncorrected from a Thomas-Hoover melting point apparatus. Ultraviolet–visible spectra were taken on a Cary 15. Infrared data are reported from a Perkin-Elmer 237. Nmr spectra were recorded on a Varian A-60 or a Bruker HFX-10. ORD–CD spectra were obtained using a Jasco ORD/UV-5 with a Sproul Scientific SS-20 CD modification.

Solvents were purified by washing with sulfuric acid, water, saturated sodium bicarbonate, and water. After drying over magnesium sulfate, they were distilled from the following drying agents: straight-chain paraffins–calcium hydride; benzene–lithium aluminum hydride; cumene–sodium. In all cases a center cut was taken and stored over molecular sieves.

***N*-(*p*-Nitrobenzenesulfonoxybenzene)sulfonamide.** Some difficulties were encountered in the synthesis outlined by Lwowski.[13] The following modified procedure similar to that used by Okahara and Swern[34] was found to be more successful.

Piloty's acid (benzenesulfamic acid) (43 g, 0.248 mol) is dissolved in 310 ml of ether and cooled to 10°. A solution of 86 g (0.388 mol) of *p*-nitrobenzenesulfonyl chloride in 320 ml of ether is added in portions, while the temperature is kept below 15°. Triethylamine (120 ml, 1.20 mol) is added dropwise at such a rate that the temperature is maintained below 15°. The solution and copious precipitate is stirred cold for 3 hr. The contents of the flask is then poured into 1200 ml of 5% hydrochloric acid. Extraction with methylene chloride, drying over magnesium sulfate, and removal of solvent at reduced pressure yield 68% of the crude product. Recrystallization can be affected from ether leaving 53 g (60%) of pure *p*-nitrobenzenesulfonoxybenzenesulfonamide.

**Sulfamide Preparation from 2-Phenyl-2-butylamine.** The previously prepared sulfonamide (46 g, 0.128 mol) is suspended in 250 ml of benzene, and tetrahydrofuran is added dropwise until dissolution is affected. The solution is cooled with an ice bath and 14.5 g (0.143 mol) of triethylamine is added dropwise with scratching and stirring. A quantitative yield of a yellow salt is obtained after stirring for 2 hr, and the salt is filtered and air dried for 0.5 hr. The salt will decompose on prolonged standing.

The semiwet salt is then dissolved in a solution of 95 g (0.64 mol) of 2-phenyl-2-butylamine[15] in 750 ml of methylene chloride, and the solution is stirred for 2 days. The solvent is stripped and the residue stirred for 2 hr with ether. A white precipitate is filtered off and discarded. The ethereal solution is washed with saturated potassium bisulfate until the aqueous layer (which contains unreacted amine hydrochloride) is acidic to hydrion paper. The organic layer is washed with water and dried over $MgSO_4$. Solvent is removed and the powdery residue is recrystallized from chloroform–cyclohexane to yield 28 g (72%) of white crystals melting at 123–124°. Basification of the aqueous layer led to recovery of 53.7 g of amine: nmr ($CDCl_3$) $\delta$ 0.75 (3 H, t), 1.8 (3 H, s), 2.0 (2 H, q), 5.2 (1 H, s), 6.5 (1 H, s), 7.3 (10 H, m); ir 3300, 1310, 1150 $cm^{-1}$.

*Anal.* Calcd for $C_{16}H_{20}N_2SO_2$: C, 63.13; H, 6.62; N, 9.20. Found: C, 63.39; H, 6.85; N, 9.39.

**1-(2-Phenyl-2-butyl)-2-phenyldiazene.** Freshly prepared sodium hypochlorite (0.31 *M*, 9 ml) is dissolved in 16 ml of 2 *N* sodium hydroxide and 50 ml of hexane is added. Sulfamide (4.08 g, 0.013 mol) is introduced and the solution is stirred under $N_2$. The temperature is allowed to rise to 35° and then to drop slowly to room temperature. The hexane layer is evaporated and the residue chromatographed on an alumina column (Woelm neutral) using 10:1 pentane–ether as eluent. Solvent removal leaves pure azo compound as a yellow oil in about 25% yield. Care must be taken to exclude any silicon grease impurity as this is quite difficult to remove: bp 98° (0.02 mm); nmr ($CCl_4$) $\delta$ 0.76 (3 H, t), 1.53 (3 H, s), 2.14 (2 H, q), 7.2–7.8 (10 H, m); visible-uv (octane) $\lambda_{max}$ 416 nm ($\epsilon$ 121), 261 (11,400); ir (neat) 1500 $cm^{-1}$.

*Anal.* Calcd. for $C_{16}H_{18}N_2$: C, 80.63; H, 7.61; N, 11.75. Found: C, 80.59; H, 7.69; N, 11.89.

**1-Cumyl-2-phenyldiazene.** By an analogous procedure cumylamine[35] gives a sulfamide in 50% yield and the corresponding azo compound in 27% yield. Sulfamide: mp 124–126°; nmr ($CDCl_3$) $\delta$ 1.69 (6 H, s), 5.20 (1 H, s), 6.7 (1 H, s), 7.2–7.4 (10 H, m).

A synthetically superior procedure is based on the scheme of Fowler.[14]

***N*-Cumyl-*N'*-phenylurea.** Cumylamine (10 g, 0.07 mol) is dissolved in 220 ml of benzene, followed by the addition of 8.8 g (0.136 mol) of phenyl isocyanate. The solution is heated to boiling for 15 min and allowed to sit overnight. White crystals (18.9 g, 99%) are collected. Recrystallization from ethanol is unnecessary for the following step, mp 190–192°.

**1-Cumyl-2-phenyldiazene.** Potassium *tert*-butoxide (3.7 g) is dissolved in 310 ml of *tert*-butyl alcohol, followed by 8.5 g (0.03 mol) of *N*-cumyl-*N'*-phenylurea. The resultant slurry is stirred for 25 min at room temperature. Freshly prepared *tert*-butyl hypochlorite[36] (7.0 g) is added dropwise over 6 min, and the temperature rises to 32°. Stirring is continued for 25 min and then the solution is poured into an ice–water mixture in a 2-l. separatory funnel. This is extracted with ether until the aqueous layer is clear. The organic layer is washed with five 1-l. portions of water, dried over potassium carbonate, and the solvent removed at reduced pressure. The red oil is extracted with pentane leaving 2.8 g of unreacted urea. The pentane is stripped and the oil chromatographed on an alumina column using 10:1 pentane–ether as eluent. As before, the first yellow band is collected and the solvent removed leaving 2.1 g of a yellow oil (46.6% based on recovered urea): bp 104° (0.09 mm); nmr ($CCl_4$) $\delta$ 1.63 (6 H, s), 7.2–7.8 (10 H, m); visible (octane) $\lambda_{max}$ 415 nm ($\epsilon$ 132.5).

The clear superiority of this latter method is demonstrated by a comparison of overall yield. The sulfamide procedure has an overall yield of 2.3% in four steps, while the urea method has an overall yield of 46% in two steps.

**1-$\alpha$,$\alpha$-Dimethylallyl-2-phenyldiazene.** The sulfamide route was employed to yield *trans*-**7** which was identical with that synthesized by the method of Baldwin, Brown, and Höfle.[37]

**1-*tert*-Butyl-2-phenyldiazene.** Synthesis of *trans*-**8** was achieved *via* the urea giving an azo compound identical with samples synthesized by a previously reported method.[38]

***cis*-1-Cumyl-2-phenyldiazene.** *trans*-**6** (1 g) is dissolved in 30 ml of pentane and the solution irradiated for 2 hr at −78° with a medium-pressure Hanovia lamp through a Pyrex filter. Nmr analysis shows that a photostationary state is attained after 2 hr which is approximately 30% cis. The mixture of cis and trans azo compounds is chromatographed on alumina using pentane followed by 10:1 pentane–ether to remove the trans, and pure ether to remove the cis. The chromatography column is cooled by refluxing isobutane (bp −0.5°) and the collection flask is immersed in a Dry Ice–acetone bath for elution of the cis. Ether is stripped on a rotary evaporator using an ice bath to heat the flask.

(34) M. Okahara and D. Swern, *Tetrahedron Lett.*, 38, 3301 (1969).

(35) A. C. Cope, T. T. Foster, and P. H. Towle, *J. Amer. Chem. Soc.*, 71, 3932 (1949).

(36) C. F. Irwin and G. F. Hennion, *ibid.*, **63**, 858 (1941).

(37) J. E. Baldwin, J. E. Brown, and G. Höfle, *ibid.*, **93**, 788 (1971).

(38) D. Y. Curtin and J. A. Ursprung, *J. Org. Chem.*, **21**, 1221 (1956).

The residue is pure *cis*-**6** which melts (decomposition) at 49–50°. Although solutions of this azo compound are unstable above 10°, once the solvent has been removed the crystalline solid may be handled routinely for short lengths of time at room temperature. It is stable indefinitely if kept in the dark at −20°: nmr ($CDCl_3$) δ 1.58 (6 H, s), 6.20 (2 H, m), 7.0–7.4 (8 H, m); visible (octane) $\lambda_{max}$ 435 nm (ε 273); ir (KBr) 1550 $cm^{-1}$.

*cis*-**1-(2-Phenyl-2-butyl)-2-phenyldiazene.** The exact same procedure yields a yellow oil which decomposes neat above 5°. It has moderate stability when stored at −20° in the dark (1 week): nmr ($CDCl_3$) δ 0.92 (3 H, t), 1.27 (3 H, s), 2.52 (2 H, q), 6.15 (2 H, m), 7.0–7.4 (8 H, m); visible (octane) $\lambda_{max}$ 435 nm (ε 279).

*cis*-**1-*tert*-Butyl-2-phenyldiazene.**[39] The above procedure yields *cis*-**8** as a yellow oil. It returns to trans slowly at room temperature but it is stable indefinitely at −20° in the dark; visible (octane) $\lambda_{max}$ 420 nm.

*cis*-**1-α,α-Dimethylallyl-2-phenyldiazene.** The standard procedure is employed with the following modifications necessitated by the extreme instability of this compound. The low-temperature chromatography column is cooled by refluxing dimethyl ether (bp −23°). The solvent ether is removed by bulb-to-bulb distillation on a vacuum line at −25°. This yellow oil is only stable for about 5 hr when stored in the dark at −20°: nmr ($CDCl_3$) δ 1.37 (6 H, s), 4.38–5.85 (3 H, m), 6.73 (2 H, m), 7.30 (3 H, m); visible (octane) $\lambda_{max}$ 415 nm.

**Product Studies.** Sample tubes were prepared using 0.15 *M* *trans*-**6** in either cumene or benzene. The solutions were freeze–pump–thaw degassed and sealed off at 0.001 mm. The tubes were photolyzed to completion at 25° with 436-nm light, frozen, and cracked. Weighed amounts of either biphenyl or naphthalene standard were introduced and the products analyzed by vpc on an F&M Model 700 gas chromatograph. Injections were made onto matched 5% high efficiency Apiezon columns programmed from 65 to 175° at 7.5°/min.

**Racemization of *trans*-1 on Partial Photolysis.** *trans*-**1** ($[\alpha]_{452}$ +336°, $[\alpha]_D$ +82°, Δε +0.34), 0.01 *M* in hexadecane, was photolyzed at 25° to 40% completion, and the remaining azo compound was recovered and purified by chromatography on alumina with 10:1 pentane–ether as eluent. Recovered **1** was shown to be uncontaminated by thin layer, ir, vis, and nmr, and had $[\alpha]_{452}$ +253°, $[\alpha]_D$ +61°, Δε +0.25 indicating optical activity about 74% that of the starting azo compound. More dilute solutions gave the same result.

*cis*-**6 Thermolysis.** Because of its stability, *cis*-**6**, could be weighed and dissolved in cold solvents with no decomposition. Solutions (0.02 *M*) were degassed and thermolyzed overnight at 25.00 ± 0.05°. Sample tubes were frozen and cracked, and the contents were quantitatively transferred to volumetric flasks which were then diluted to the mark. Visible spectra were taken and the percentage yield of trans calculated.

*cis*-**1 Thermolysis.** Solutions (0.05 *M*) of *cis*-**1**, of known optical purity, were prepared and thermolyzed overnight at 25.00 ± 0.05°. The tubes were frozen and cracked, and the contents were chromatographed on alumina. *trans*-**1** was isolated, and heptane solutions of it were analyzed by visible and CD spectra.

**Quantum Yields.** Solutions (0.03 *M*) of **1** were frozen, pumped, thawed, and degassed in 2-cm matched Pyrex tubes. Photolyses were carried out on a merry-go-round apparatus using a medium-pressure Hg lamp filtered to transmit 436-nm light. Several tubes containing **1** in different solvents along with ferrioxolate actinometer tubes were photolyzed for a specified time period. The tubes containing **1** were allowed to stand 2 hours at 25° and diluted 1 to 5. **1** remaining was determined by uv analysis.

**Acknowledgments.** We gratefully acknowledge the expert synthetic assistance offered by Mr. Craig Rice and Mr. William Stewart.

(39) This sample is identical with one in an earlier report: S. N. Ege and R. R. Sharp, *J. Chem. Soc. B*, 2014 (1971).

# Photoreactions of Transition Metal Complexes. Ligand Reactivity as a Probe for Excited-State Characterization[1]

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**Abstract:** An investigation of the photochemistry of a series of ruthenium(II)–4-stilbazole complexes is reported. The complexes under investigation, $[Ru(2,2'\text{-bipy})_2(trans\text{-4-stilbazole})_2]^{2+}$ (**1**), $[Ru(2,2'\text{-bipy})_2(cis\text{-4-stilbazole})_2]^{2+}$ (**2**), $[Ru(2,2'\text{-bipy})_2(trans\text{-4-stilbazole})Cl]^{+}$ (**3**), and $[Ru(2,2'\text{-bipy})_2(cis\text{-4-stilbazole})Cl]^{+}$ (**4**), undergo wavelength-dependent isomerization of the stilbazole ligand as their only important photoreaction under direct or sensitized irradiation in butyronitrile. A study of the details of the ligand cis → trans isomerization as a function of wavelength has demonstrated the reactivity of at least two different types of excited states that can serve as reactive intermediates. Irradiation into long wavelength transitions of these complexes generates charge-transfer excited states which appear best described as metal–oxidized-ligand radical anions. Activation with higher energy light produces states which appear very similar in behavior to the lowest excited states of the free ligand. In this case it appears that the wavelength effects are due to rapid reaction of the upper excited states instead of to slow radiationless processes.

Recent studies of the photochemistry of transition metal complexes and organometallic compounds have revealed a wide variety of interesting photoreactions including redox phenomena, ligand substitution, and isomerizations involving in various cases either or both complex and ligand.[3–6] In contrast to many organic systems, the inorganic complexes offer a rich array of possible excited states and to date characterization of the various excited states as to identity, lifetime, or reactivity has been limited. The common observation of wavelength effects here as compared with most organic molecules has raised questions as to whether radiationless processes are generally slower for

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(2) Alfred P. Sloan Foundation Fellow.

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