

# Syntheses and Photochemistry of Eight-Membered Cyclic Azo Compounds<sup>1</sup>

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**Abstract:** The preparation of the *cis* and *trans* isomers of 3,8-dimethyl-*cis*-1,2-diaza-1-cyclooctene (**1** and **2**, R = CH<sub>3</sub>) and the synthesis of *cis*-1,2-diaza-1-cyclooctene (**3**) are described. The irradiation of these compounds and of *trans*-1,2-diphenyl-*cis*-1,2-diaza-1-cyclooctene (**2**, R = C<sub>6</sub>H<sub>5</sub>) in the presence and in the absence of triplet sensitizers is also discussed. In all cases, differences in the amounts of disproportionation and coupled products were noted when product distributions observed in the sensitized reactions were compared with those of the nonsensitized photolyses. These variations in product ratios were rationalized in terms of spin-correlation effects.

Recently, there has been considerable interest in the mechanistic details of the photochemical decompositions of aliphatic acyclic<sup>4,5</sup> and cyclic<sup>6-10</sup> azo compounds. Of particular significance have been the product distributions obtained from direct and sensitized photolyses of the smaller ring azo derivatives. Variations in the product ratios of these materials have been attributed to differences in reactivity between the singlet- and triplet-state diradicals generated in the two photochemical processes. Such differences in reactivity have been referred to as spin-correlation effects.<sup>4</sup> These effects, although not as yet observed in any irradiation studies of linear aliphatic azo compounds,<sup>4</sup> have been reported for the more strained five- and six-membered cyclic azo compounds.<sup>6,7,9</sup>

Recently, we have initiated a program to study possible spin-correlation effects in the larger ring azo derivatives, *i.e.*, the eight-, nine-, ten-, and eleven-membered rings. In these cases, transannular reactions can occur and the azo linkages are under considerably less strain than in the smaller size rings. It was of interest to determine what effect these factors would have on the photochemical behavior of large ring compounds in the presence and absence of triplet-state sensitizers. In this report are described our investigations of the photochemistry of some eight-membered cyclic azo compounds which constitute the first member of this series.

## Results and Discussion

**Synthesis and Structure Proof.** The synthetic route previously employed for the preparation of 3,8-diaryl eight-membered azo compounds (**1** and **2**, R = C<sub>6</sub>H<sub>5</sub>)

(1) This is the 47th in a series of papers concerned with the preparation and decomposition of azo compounds. For the previous paper, see C. G. Overberger, J. W. Stoddard, C. Yaroslavsky, H. Katz, and J.-P. Anselme, *J. Amer. Chem. Soc.*, **91**, 3226 (1969).

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(3) Abstracted from the Ph.D. Dissertation of John W. Stoddard, The University of Michigan, 1969.

(4) P. D. Bartlett and P. S. Engel, *J. Amer. Chem. Soc.*, **90**, 2960 (1968).

(5) I. Abram, G. Milne, B. Solomon, and C. Steel, *ibid.*, **91**, 1220 (1969).

(6) P. D. Bartlett and N. A. Porter, *ibid.*, **90**, 5317 (1968).

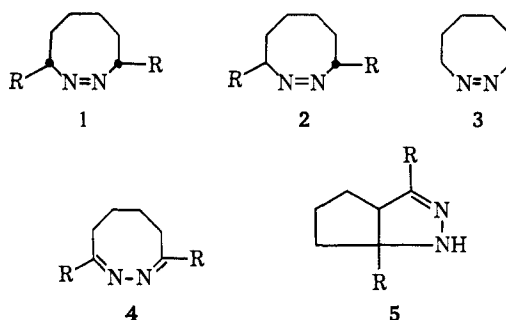
(7) S. D. Andrews and A. C. Day, *Chem. Commun.*, 667 (1966).

(8) R. Moore, A. Mishra, and R. J. Crawford, *Can. J. Chem.*, **46**, 3305 (1968).

(9) C. DeBoer, Ph.D. Dissertation, California Institute of Technology, 1966.

(10) C. G. Overberger, J. W. Stoddard, C. Yaroslavsky, H. Katz, and J.-P. Anselme, *J. Amer. Chem. Soc.*, **91**, 3226 (1969).

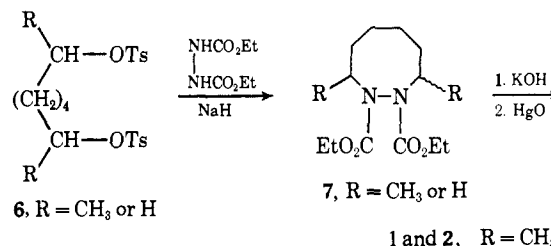
or *p*-MeOC<sub>6</sub>H<sub>4</sub>) involved the condensation of the corresponding 1,6-diaryl ketones with hydrazine to give cyclic azines **4** (R = C<sub>6</sub>H<sub>5</sub> or *p*-MeOC<sub>6</sub>H<sub>4</sub>).<sup>10</sup>



Subsequent hydrogenation of these compounds followed by mercuric oxide oxidation of the intermediate hydrazines afforded the desired azo isomers **1** and **2** (R = C<sub>6</sub>H<sub>5</sub> or *p*-MeOC<sub>6</sub>H<sub>4</sub>). However, when a similar approach was used to prepare the 3,8-dimethylazine **4** (R = CH<sub>3</sub>) utilizing 2,7-octanedione for the initial condensation reaction, the product isolated was the bicyclic hydrazine **5** (R = CH<sub>3</sub>), presumably generated *via* an intramolecular aldol condensation.<sup>11,12</sup>

The syntheses of **1** and **2** (R = CH<sub>3</sub>) and of **3** were accomplished using the route outlined in Scheme I.

## Scheme I



Addition of *sym*-dicarbethoxyhydrazine to the appropriately substituted ditosylate **6**<sup>13</sup> in refluxing

(11) J. Kossanyi, *Comp. Rend.*, **257**, 929 (1963).

(12) J. Kossanyi, *Bull. Soc. Chim. France*, 722 (1965).

(13) The cyclization to **7** (R = H) was effected in slightly higher yields using 1,6-dibromohexane; however, the reaction gave only trace amounts of **7** (R = CH<sub>3</sub>) when 2,7-dibromooctane was used as the coupling reagent. The seven-membered analog of **7** (R = H) was prepared previously using 1,5-dibromopentane, potassium metal, and DMF as a solvent [G. Sinner and W. Deucher, *Arch. Pharm. (Weinheim)*, **7**, 526 (1962)]. The use of their method, however, failed in the case of the eight-membered derivative **7** (R = H).

diglyme afforded the eight-membered cyclic adducts **7** ( $R = H$  and  $CH_3$ ) in 20 and 9% yields, respectively. Sodium hydride was used as a base and reaction times ranged between 70 and 150 hr. Hydrolysis of the carboxy groups of **7** ( $R = H$ ) with potassium hydroxide and subsequent oxidation of the intermediate hydrazine gave **3** in high yield. In a similar fashion, a mixture of *cis*- and *trans*-3,8-dimethyl azo isomers (**1** and **2**,  $R = CH_3$ ) was formed from **7** ( $R = CH_3$ ). The diastereomers (**1** and **2**,  $R = CH_3$ ), which were readily distinguished by nmr because of the chemical-shift nonequivalence of the C-methyl groups, were separated by column chromatography over Florisil.

The structures of isomers **1** and **2** ( $R = CH_3$ ) and of **3** were confirmed by nmr, ir, uv, and elemental analyses. The azo linkages were assigned the *cis* configuration on the basis of their uv absorption at 389 (**1** and **2**,  $R = CH_3$ ) and 387  $m\mu$  (**3**) in isoctane. These data are analogous to the absorption maxima observed for  $\alpha,\alpha'$ -dialkyl<sup>14</sup> and tetraalkyl<sup>6</sup> substituted *cis*-azo six-membered and  $\alpha,\alpha'$ -diaryl-substituted *cis*-azo six-,<sup>15</sup> seven-,<sup>16</sup> and eight-membered (**1**,  $R = C_6H_5$  and *p*-MeOC<sub>6</sub>H<sub>4</sub>)<sup>10</sup> cyclic compounds.

The configurations of the methyl groups of **1** and **2** ( $R = CH_3$ ) have been tentatively assigned as *cis* and *trans*, respectively. This assignment was based on a comparison of the differences in chemical properties of these two isomers with those same differences exhibited by *cis*- and *trans*-3,8-diaryl-1,2-diaza-1-cyclooctenes (**1** and **2**,  $R = C_6H_5$  and *p*-MeOC<sub>6</sub>H<sub>4</sub>).<sup>10</sup> For example, isomer **2** ( $R = CH_3$ ) isomerized slower to hydrazone in base and was more thermally stable and more soluble in hydrocarbon solvents than isomer **1** ( $R = CH_3$ ). These are patterns which are similar to those exhibited by the diaryl analogs.<sup>17</sup>

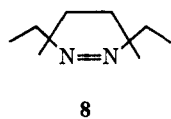
**Photochemistry.** Over the past several years, intensive studies have been involved with the direct comparisons of the photochemistry of both the singlet and triplet states of organic molecules.<sup>18</sup> The products or product ratios in most cases differ between the two reactions. In compounds where triplet states have been difficult to obtain because of poor intersystem-crossing efficiencies or very high singlet-excitation energies, photosensitizers have provided an effective method for exciting these molecules to triplet-state species.

Triplet-energy transfer has only recently been effected in certain five- and six-membered cyclic azo compounds.<sup>6,9</sup> In these cases, photochemical decomposition in the presence of a triplet sensitizer gave products whose yields differed from those observed for the products formed during the corresponding nonsensitized photolyses. For example, *meso*- and

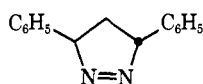
*d,l*-**8** on direct irradiation gave as the predominant product the cyclobutane derivative with essentially complete retention of configuration in each case. On the other hand, triplet-sensitized irradiation in the presence of thioxanthone led to a decrease in coupled-product stereoselectivity as well as to an increase in 2-methyl-1-butene.<sup>6</sup> In a similar fashion, *trans*-3,5-diphenyl-1-pyrazoline (**9**) resulted in less *trans*-1,2-diphenylcyclopropane after photosensitized irradiation than was obtained from direct photolysis.<sup>9</sup> These variations in product distribution between the direct and indirect photolytic processes have been attributed to the differences in reactivity between intermediate diradicals whose spins are coupled and the corresponding diradicals having uncoupled spins (singlet- and triplet-radical pairs). In the singlet-state diradical, electron spins are antiparallel and immediate bond formation between the electron pair can occur. Consequently, the stereochemistry at the  $\alpha$ -carbon of the initial cyclic azo compound is preserved in the corresponding coupled product. On the other hand, when the electron spins are parallel, spin inversion must take place prior to bonding between the radical pair. In these cases, some bond rotation usually takes place at the radical center before spin inversion and a loss of configuration at the  $\alpha$ -carbons is thus observed in the coupled products. More importantly, the longer lived triplet diradical allows more time for the occurrence of other competing intramolecular processes such as secondary carbon-carbon bond cleavages<sup>6</sup> or disproportionation which do not depend upon direct bonding between the intermediate diradicals. It is interesting to note that the acyclic aliphatic azo derivatives undergo *trans*-*cis* nitrogen-nitrogen bond isomerization rather than decomposition when irradiated in the presence of benzophenone and do not exhibit spin correlation effects. Cyclic azo compounds, on the other hand, decompose readily under both direct and indirect photolyses and in general show different product distributions between the two reactions. This difference in behavior between linear and small ring azo compounds has been attributed to the extra strain and structural rigidity associated with the azo linkage as a result of its incorporation into the five- and six-membered rings.<sup>4</sup>

An investigation of the direct- and triplet-sensitized photolyses of eight-membered cyclic azo compounds was undertaken in order to study possible spin correlation effects in a larger, more flexible ring system. The reaction patterns of these substances differed from those of the five- and six-membered cyclic analogs, and are a direct consequence of the larger ring structure in which transannular reactions can occur. In addition, the azo linkages, although still *cis*, are under considerably less strain than in the smaller, more rigid ring systems, and this may be another factor responsible for the products observed. In each instance, decomposition of the azo linkage was the only reaction that occurred (no  $-N=N-$  isomerization was observed) in both sensitized and nonsensitized processes, and differences were noted in the product ratios between the two photochemical reactions.

The major process occurring during solid-state irradiation of *cis*- and *trans*-3,8-diaryl-1,2-diaza-1-cyclooctenes (**1** and **2**,  $R = C_6H_5$ ) was disproportion-



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(14) S. G. Cohen and R. Zand, *J. Amer. Chem. Soc.*, **84**, 586 (1962).

(15) S. G. Cohen, S. Hsalo, E. Saklad, and C. H. Wang, *ibid.*, **79**, 2661, 4400 (1957).

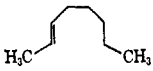
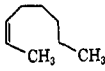


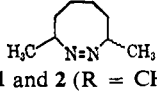
(16) C. G. Overberger and J. Lombardino, *ibid.*, **80**, 2317 (1958).

(17) Explanations for these differences in behavior between *cis*- and *trans*-3,8-diaryl isomers **1** and **2** ( $R = C_6H_5$  or *p*-MeOC<sub>6</sub>H<sub>4</sub>) are given in ref 10.

(18) P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 21 (1968).



Table II. Direct and Sensitized Photolyses of 1 and 2<sup>a</sup>

Source	Sensitizer, 6 M excess	Relative percentage yields			
		 13	 14		
 1 and 2 (R = CH <sub>3</sub> )	None	47.5	25.5	24.0	3.0
	Fluorene	58.0	29.0	11.3	1.7
	Benzophenone	Trace	Trace	0	0

<sup>a</sup> All runs at 19° for 168 hr in THF; 450:50 mixture, R = CH<sub>3</sub>.

direct photolyses were inconsistent with those found for either 8 or 9.

A mixture (50:50) of *cis*- and *trans*-3,8-dimethyl-*cis*-1,2-diaza-1-cyclooctenes (1 and 2, R = CH<sub>3</sub>) exhibited a spin-correlation effect when irradiated in the presence and in the absence of nonketonic triplet sensitizers. The product distribution data from the two photodecompositions are summarized in Table II. The products were shown to be photostable under the conditions employed and their concentrations were determined from a comparison of product peak areas (glpc) with those areas found by injecting known concentrations of authentic samples. The increase in yields of the olefinic compounds (13 and 14) in the sensitized reaction, again suggests the formation of a longer lived triplet 1,6-diradical species in which more time is allowed for intramolecular hydrogen transfer to occur, a process not dependent on the direct coupling of the two radicals as is the case in the formation of coupled products. Furthermore, the decrease in the stereoselective formation of *trans*-1,2-dimethylcyclohexanes is also consistent with the expected longer lifetime of a triplet diradical. In this case, further bond rotation is possible during the time required for spin inversion to occur, and consequently, the ratio of *trans*- to *cis*-dimethylcyclohexane would be expected to decrease. The variations in the relative amounts of *trans*- and *cis*-2-octenes (13 and 14) as compared to the relative amounts of *trans*- and *cis*-dimethylcyclohexanes (Table II) produced in both the direct and indirect photochemical reactions may indicate the presence of a 1,2-triplet hexylene diradical formed subsequent to the transfer of a hydrogen atom in the disproportionation process. This possibility is being further investigated by irradiation studies of the two separate isomers 1 and 2 (R = CH<sub>3</sub>) under sensitized and nonsensitized conditions.

### Experimental Section<sup>22</sup>

**1,2-Dicarbethoxy-1,2-diazacyclooctane (7, R = H).** To a 1-l. three-necked flask equipped with a mechanical stirrer, reflux condenser topped with a drying tube, and pressure equalizer dropping funnel was added 300 ml of diglyme (distilled from lithium aluminum hydride) and 9.3 g (0.233 mol) of sodium hydride (60.1% mineral oil dispersion). With vigorous stirring, 42 g (0.238 mol) of *sym*-dicarbethoxyhydrazine dissolved in 50 ml of diglyme was

added at a rate slow enough to avoid excess foaming. After the evolution of hydrogen had stopped, 58 g (0.238 mol) of freshly distilled 1,6-dibromohexane was added. The dropping funnel was replaced with a thermometer (ground-glass joint). The white mixture was heated slowly to 135° and rapidly stirred for 15 hr. The temperature was then reduced to 110° by the addition of 350 ml more of dry diglyme. To this diluted solution was added carefully 2 additional equiv (18.6 g, 0.466 mol) of sodium hydride dispersion slow enough to avoid excess effervescence. The heterogeneous solution, which then turned light brown, was heated at 162° for 80 hr. The mixture was then cooled to room temperature and filtered. To this filtrate was added 150 ml of water and the resulting solution was extracted with 2 l. of ether and 500 ml of chloroform. The combined organic portions were dried over magnesium sulfate. The solution was filtered and the ether-chloroform removed *in vacuo*; the diglyme was removed by distillation at 62° (15 mm). The remaining oil was fractionally distilled to yield 13.9 g (22%) of X (R = H): bp 100–105° (0.005 mm); *n*<sup>20</sup><sub>D</sub> 1.4625; nmr (CCl<sub>4</sub>)  $\tau$  6.0 quartet (4 H, OCH<sub>2</sub>CH<sub>3</sub>), 6.6 multiplet (4 H, CH<sub>2</sub>-N), 8.4 singlet (8 H, CH<sub>2</sub>), 8.7 triplet (6 H, OCH<sub>2</sub>CH<sub>3</sub>); infrared (neat) 5.85  $\mu$  (C=O).

*Anal.* Calcd for C<sub>12</sub>H<sub>22</sub>N<sub>2</sub>O<sub>4</sub>: C, 55.80; H, 8.58; N, 10.85. Found: C, 55.84; H, 8.57; N, 10.79.

**1,6-Hexane Ditosylate (6, R = H).** To a cooled solution (0°) of 500 ml of pyridine and 194 g (1.020 mol) of *p*-toluenesulfonyl chloride was added 50 g (0.423 mol) of 1,6-hexanediol. The mixture was mechanically stirred for 5.5 hr at 0° and then poured over crushed ice. The precipitate was collected and washed with water. Recrystallization from methanol gave 164 g (90%) of ditosylate 6 (R = H), mp 72.5–74.0° (lit.<sup>23</sup> mp 71–72°).

*Anal.* Calcd for C<sub>20</sub>H<sub>26</sub>O<sub>6</sub>S<sub>2</sub>: C, 56.33; H, 6.14. Found: C, 56.44; H, 6.14.

**1,2-Dicarbethoxy-1,2-diazacyclooctane (7, R = H) via 1,6-Hexane Ditosylate.** The procedure followed in this case was similar to that described above for the preparation of 7 (R = H) using 1,6-dibromohexane. The cyclization reaction, however, with 1,6-hexane ditosylate as the coupling reagent was complete in only 70 hr at 120° in yields between 18 and 20%.

**1,2-Diazacyclooctane.** A solution of 10 g (0.0383 mol) of 1,2-dicarbethoxy-1,2-diazacyclooctane (7, R = H) dissolved in 50 ml of methanol was mixed with 12 g (0.210 mol) of potassium hydroxide. The mixture was refluxed for 24 hr under an atmosphere of nitrogen. At the end of this time, 8 g (0.140 mol) of additional potassium hydroxide was added and the mixture was refluxed for 40 more hr. The solution was cooled, filtered, mixed with 200 ml of ether (sodium dried), and dried over potassium carbonate-magnesium sulfate. The dried solution was refiltered and evaporated at room temperature using water aspirator pressure. When the pressure reached 15 mm, the remaining liquid was redissolved into 200 ml of ether, dried over potassium carbonate-magnesium sulfate, and the ether evaporated *in vacuo* at room temperature. The residual oil was fractionally distilled under a nitrogen atmosphere and furnished 2.68 g (76%) of eight-membered cyclic hydrazine: bp 71–74° (15 mm); nmr (CCl<sub>4</sub>)  $\tau$  6.22 singlet (2 H, NH), 7.25 multiplet (4 H, CH<sub>2</sub>-N), 8.42 singlet (8 H, CH<sub>2</sub>); infrared (neat) 3.02  $\mu$  (NH).

*Anal.* Calcd for C<sub>8</sub>H<sub>14</sub>N<sub>2</sub>: C, 63.11; H, 12.35. Found: C, 62.94; H, 12.16.

**1,2-Diaza-1-cyclooctene (3, R = H).** To 2.0 g (0.172 mol) of freshly distilled and analytically pure 1,2-diazacyclooctane (hydrazine) in 30 ml of tetrahydrofuran (distilled from lithium alumi-

(22) Boiling points and melting points are uncorrected. Refractive indexes were obtained on an Abbe refractometer (Spencer) 1747. Microanalyses were performed by Spang Microanalytical Lab., Ann Arbor, Mich. Infrared spectra were determined with a Perkin-Elmer Model 237 infrared spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Varian Model A-60 spectrometer using tetramethylsilane as an internal standard. Ultraviolet spectra and isomerization data were obtained with a Perkin-Elmer Model 202 ultraviolet spectrophotometer.

(23) E. J. Fear, J. Thrower, and J. Veitch, *J. Chem. Soc.*, 1322 (1958).

num hydride) was added 30 g (0.312 mol) of mercuric oxide (yellow powder) and 1.0 g of anhydrous magnesium sulfate. The mixture was stirred magnetically under a nitrogen atmosphere for 48 hr. The brown mixture was then filtered (Celite) *in vacuo* within a closed system. The vacuum was released by the admission of anhydrous nitrogen gas. The tetrahydrofuran was removed under water aspirator pressure at room temperature. Removal of the final traces of solvent by applying 0.01-mm pressure for 20 min at room temperature led to 1.5 g (81%) of analytically pure diazacyclooctene **3** ( $R = H$ ):  $n_D^{25}$  1.4891; nmr ( $CCl_4$ )  $\tau$  5.96 unsym triplet (4 H,  $CH_2-N$ ), 8.35 multiplet (4 H  $CH_2CH_2-N$ ), 8.78 multiplet (4 H,  $CH_2-(CH_2)_2N$ );  $\lambda_{max}^{isooctane}$  389 m $\mu$  ( $\epsilon$  110); infrared (neat) 6.4  $\mu$  ( $-N=N-$ ).

*Anal.* Calcd for  $C_8H_{12}N_2$ : C, 64.27; H, 10.69. Found: C, 64.24; H, 10.78.

**2,7-Octanediol.** Into a three-necked flask equipped with a dropping funnel, thermometer, and mechanical stirrer (flame dried) was siphoned 700 ml of a solution of tetramethylenedimagnesium bromide dissolved in ether (1 mol/l., Peninsular Chemresearch, Inc.). The temperature was lowered to 12° and was controlled by cooling the flask in ice-water. To the rapidly stirred solution, 2 equiv of acetaldehyde was added dropwise at a rate slow enough to keep the reaction temperature below 15°. The addition took 5 hr. The reaction mixture was then stirred for an additional 30 min and carefully poured over 600 ml of crushed ice and water. Concentrated hydrochloric acid was added in small amounts until the solution cleared. The acidic solution was extracted with three (500 ml) portions of ether, and the organic layers dried over potassium carbonate. The ethereal extract was filtered and concentrated *in vacuo*. The remaining oil was fractionally distilled affording 30.0 g (25%) of the diol: bp 138–140° (15 mm), lit.<sup>24</sup> bp 138–139° (14 mm); nmr ( $CCl_4$ )  $\tau$  5.5 singlet (2 H, OH), 6.3 multiplet (2 H, CH), 8.65 singlet (8 H,  $CH_2$ ), 8.9 doublet (6 H,  $CH_3-CH$ ); infrared (neat) 3.1  $\mu$  (OH).

*Anal.* Calcd for  $C_8H_{18}O_2$ : C, 65.71; H, 12.41. Found: C, 65.76; H, 12.51.

**2,7-Octane Ditosylate (6,  $R = CH_3$ ).** To a solution of 20 g (0.137 mol) of 2,7-octanediol dissolved in 200 ml of pyridine at 0° was added slowly 63.0 g (0.548 mol) of *p*-toluenesulfonyl chloride. The reaction was stirred for 4 hr at 0° and allowed to stand in the refrigerator overnight. The solution was then poured over ice and the resulting precipitate filtered with suction. The semisolid (55 g, 89%), although difficult to recrystallize, was homogeneous on thin layer chromatography (silica gel–10% methanol in benzene) and therefore was used without further purification. Characteristic infrared bands appeared at 8.5 and 7.2  $\mu$ ; nmr ( $CCl_4$ )  $\tau$  2.52 two doublets (8 H,  $C_6H_4-$ ), 5.5 unresolved multiplet (2 H,  $CH-O$ ), 7.6 singlet (6 H,  $O-CH_3$ ), 8.81 doublet (6 H,  $C-CH_3$ ).

***cis*- and *trans*-3,8-Dimethyl-1,2-dicarboxy-1,2-diazacyclooctanes (7,  $R = CH_3$ ).** To a three-necked flask equipped with a mechanical stirrer, thermometer, and reflux condenser was added 400 ml of diglyme (distilled from lithium aluminum hydride). The solution was rapidly stirred during the addition of 4.91 g (0.123 mol) of sodium hydride dispersion. To the white mixture was then added slowly 21.6 g (0.123 mol) of *sym*-dicarbethoxyhydrazine and 55.0 g (0.121 mol) of 2,7-octane ditosylate **6** ( $R = CH_3$ ). The reaction mixture was heated slowly with an oil bath until the temperature reached 80° and then heated overnight at 95°. The solution was cooled to 80° by the addition of 350 ml of diglyme, and 9.8 g of NaH (0.246 mol of sodium hydride dispersion) was added slowly. The final mixture was heated at 120° for 144 hr. The temperature of the reaction was increased to 155° and the mixture stirred for 72 additional hr. The solution was cooled to room temperature and filtered with suction. After the addition of 100 ml of water, the mixture was extracted with 2 l. of ether. The organic layer was dried over magnesium sulfate and the ether removed on a rotary evaporator. The excess diglyme was removed by distillation at 62° (15 mm). A fractional distillation of the resultant brown oil afforded 3.2 g (9%) of the diastereomeric mixture **7** ( $R = CH_3$ ): bp 85–90° (0.005 mm),  $n_D^{25}$  1.4665; nmr ( $CCl_4$ )  $\tau$  6.0 quartet (8 H,  $OCH_2-CH_3$ ), 6.0 unresolved multiplet (4 H,  $CH_3CH-N$ ), 8.7 (4 OH,  $CH_3-CH$  and  $-CH_2-$ ); infrared (neat) 5.81 ( $C=O$ ), 7.2  $\mu$  ( $C-CH_3$ ).

*Anal.* Calcd for  $C_{14}H_{26}O_4N_2$ : C, 58.71; H, 9.15; N, 9.78. Found: C, 58.83; H, 9.19; N, 9.71.

***cis*- and *trans*-3,8-Dimethyl-1,2-diazacyclooctane.** A mixture of 3.2 g (0.010 mol) of diethyl hydrazodicarboxylate **7** ( $R = CH_3$ ) and 2.71 g (0.0484 mol) of potassium hydroxide in 22 ml of meth-

anol was refluxed under a nitrogen atmosphere for 48 hr. Without cooling, an additional 4 equiv of potassium hydroxide was added and the reflux continued for an additional 48 hr. The alcoholic solution was then cooled to room temperature and filtered through Celite after the addition of 100 ml of dry ether. The resultant ethereal-alcohol mixture was dried over magnesium sulfate, filtered, and evaporated in an atmosphere of nitrogen at room temperature until the aspirator pressure reached 15 mm. The semi-solid remaining was extracted with two (100-ml) portions of ether (dried with sodium wire), dried, and the ether evaporated at room temperature. Fractional distillation of the residual oil gave 1.2 g (79%) of the colorless, 3,8-dimethyl cyclichydrazine: bp 95–97° (15 mm); nmr ( $CCl_4$ )  $\tau$  7.0 singlet (4 H, NH), 7.25 multiplet (4 H,  $CH-CH_3$ ), 8.47 (16 H,  $CH_2$ ), 9.05 doublet (6 H,  $CH_3-CH$ ,  $J = 1$  Hz), 9.16 doublet (6 H,  $CH_3-CH$ ,  $J = 1$  Hz); infrared (neat) 3.05 (NH), 7.2  $\mu$  ( $C-CH_3$ ).

*Anal.* Calcd for  $C_8H_{18}N_2$ : C, 67.54; H, 12.75. Found: C, 67.48; H, 12.62.

**Synthesis and Separation of *cis*- and *trans*-3,8-Dimethyl-1,2-diaza-1-cyclooctenes (1 and 2,  $R = CH_3$ ).** To 1.0 g (7.0 mmol) of a mixture of *cis*- and *trans*-3,8-dimethyl-1,2-diazacyclooctane (hydrazines) dissolved in 25 ml of tetrahydrofuran (distilled from lithium aluminum hydride) was added 10 g (0.104 mol) of mercuric oxide (yellow powder) and 0.5 g of magnesium sulfate. The mixture was stirred magnetically for 48 hr under a nitrogen atmosphere. The solution was filtered through Celite under vacuum in a closed system, and when filtration was complete, the vacuum was released in a nitrogen atmosphere. Removal of the tetrahydrofuran *in vacuo* at room temperature afforded 0.7 g (83%) of a mixture (50:50, as indicated by nmr) of isomers **1** and **2** ( $R = CH_3$ ): nmr ( $CCl_4$ )  $\tau$  6.15 multiplet (2 H,  $CH-CH_3$ ), 6.40 multiplet (2 H,  $CH-CH_3$ ), 8.32 multiplet (16 H,  $CH_2$ ), 8.46 doublet (6 H,  $CH_3CH$ ,  $J = 6$  Hz), 8.52 doublet (6 H,  $CH_3CH$ ,  $J = 6$  Hz), infrared (neat) 6.4 ( $-N=N-$ ) and 7.2  $\mu$  ( $C-CH_3$ );  $\lambda_{max}^{isooctane}$  389 ( $\epsilon$  101).

The separation of isomers **1** and **2** ( $R = CH_3$ ) was effected by the chromatography of the mixture over Florisil (Floridin Corp., Pittsburgh, Pa.). To the diastereomeric mixture of **1** and **2** ( $R = CH_3$ ) was added 2 ml of petroleum ether (30–60°) which caused the partial precipitation of isomer **1** ( $R = CH_3$ ). The entire solution was passed over a 1.2  $\times$  10 cm column of Florisil. The soluble isomer **2** ( $R = CH_3$ ) was eluted with the first 30 ml of petroleum ether. Isomer **1** ( $R = CH_3$ ) was removed by further elution with a 20% ether-petroleum ether solution. Isomer **2** ( $R = CH_3$ ) showed the following: nmr ( $CCl_4$ )  $\tau$  6.40 multiplet (2 H,  $CHCH_3$ ), 8.32 multiplet (8 H,  $CH_2$ ), 8.46 doublet (6 H,  $CH_3CH$ ,  $J = 6$  Hz).

*Anal.* Calcd for  $C_8H_{10}N_2$ : C, 68.51; H, 11.50; N, 19.90. Found: C, 68.35; H, 11.48; N, 19.91.

Isomer **1** ( $R = CH_3$ ) showed the following: nmr ( $CCl_4$ )  $\tau$  6.15 multiplet (2 H,  $CHCH_3$ ), 8.32 multiplet (8 H,  $CH_2$ ), 8.52 doublet (6 H,  $CH_3CH$ ,  $J = 6$  Hz).

*Anal.* Calcd for  $C_8H_{10}N_2$ : C, 68.51; H, 11.50; N, 19.90. Found: C, 68.31; H, 11.40; N, 20.04.

**Rates of Isomerization of Isomers 1 and 2 ( $R = CH_3$ ).** A comparison of the rates of isomerization of **1** and **2** was made in dilute basic isopropyl alcohol solution by observing the increase of hydrazone formation at 260 m $\mu$ . The rates of isomerization of both compounds were very slow under these conditions; however, isomer **1** was found to isomerize approximately 30 times faster than the *trans*-isomer **2**.

***trans*-3,8-Diphenyl-1,2-diaza-1-cyclooctene (2,  $R = C_6H_5$ ).** Compound **2** ( $R = C_6H_5$ ) was prepared according to the procedure described in ref 10, mp 90–91°, lit.<sup>10</sup> 90–91°.

**Direct and Sensitized Photolyses (General).** All photochemical reactions were carried out in 7  $\times$  200 mm cylindrical Pyrex tubes held in a vertical position against a water-cooled quartz insert containing an immersion-type Hanovia medium-pressure 450-W mercury arc lamp. The tubes were cooled by submerging them in ethanol cooled by copper coils with tap water (or ice-water) running through them. A nitrogen atmosphere was provided by connecting the tubes by means of tygon tubing to a nitrogen-flow apparatus. The tetrahydrofuran used was distilled from lithium aluminum hydride. Vapor phase chromatography was carried out with an F & M Model 600 using a thermal conductivity detector and helium as the carrier gas.

**Direct and Sensitized Photolyses of *cis*-1,2-Diaza-1-cyclooctene (3).** The results of the irradiation of **3** under direct and sensitized conditions are tabulated in Table I. In a typical experiment, each Pyrex tube contained 54 mg (0.482 mmol) of **3** dissolved in 1 ml of tetrahydrofuran. To tubes to be sensitized were also added appropriate amounts of sensitizers. As a control, a tube containing

(24) T. R. Marshall and W. H. Perkin, *J. Chem. Soc.*, 241 (1890).

a 1:1 mixture of 1-hexene and cyclohexane in tetrahydrofuran (with and without sensitizers) was irradiated at the same time. The samples were photolyzed for 168 hr at 27°. The reaction products were analyzed without solvent removal on a 6-ft column of 20% SF-96 on Chromsorb P at 50°. The concentrations of 1-hexene and cyclohexane formed in the two photochemical transformations were determined by comparisons of product peak areas (glpc) with those of known concentrations of the two hydrocarbons. Injection of known concentrations of 1-hexene and cyclohexane indicated 90% reaction after 168 hr.

**Direct and Sensitized Photolyses of *cis*- and *trans*-3,8-Dimethyl-1,2-diaza-1-cyclooctenes 1 and 2 (R = CH<sub>3</sub>).** The results of the irradiation studies of mixtures of 1 and 2 (R = CH<sub>3</sub>) under direct and photosensitized conditions are given in Table II. These experiments were conducted in the same fashion as for *cis*-1,2-diaza-cyclooctene (3). In this case, the concentration of 1 and 2 (R = CH<sub>3</sub>) was 45 mg (0.300 mmol) in 1 ml of solution. After 345 mg (2.08 mmol) of fluorene was added to one tube, the samples were irradiated for 168 hr at 19°. Analyses (glpc) of the hydrocarbon mixtures were performed on a 6-ft column of 20% SF-96 on Chrom-

sorb P at 25° and on a 6 ft column of 5% QF-1 on Chromsorb W at 45° without solvent removal. Concentrations of products were determined from comparisons of peak areas with those obtained by injections of known amounts of the four hydrocarbons.

**Direct and Sensitized Photolyses of *trans*-3,8-Diphenyl-1,2-diaza-1-cyclooctene 2 (R = C<sub>6</sub>H<sub>5</sub>).** The photochemical reactions of 2 (R = C<sub>6</sub>H<sub>5</sub>) were conducted as that described above. Into each of two Pyrex tubes containing 2 ml of tetrahydrofuran was added 57 mg (0.232 mmol) of *trans*-3,8-diphenyl-1,2-diaza-1-cyclooctene 2 (R = C<sub>6</sub>H<sub>5</sub>). The samples were irradiated at 0° for 37 hr after 83 mg (0.460 mmol) of benzophenone had been added to one of the tubes. The photolytic solutions were analyzed on a 6-ft FFAP column at 220°. Comparisons of retention times were made with those of authentic samples.<sup>10</sup> Ultraviolet analyses of irradiated samples of 2 (R = C<sub>6</sub>H<sub>5</sub>) at different time intervals indicated no *cis*→*trans* isomerization of the azo linkage taking place.

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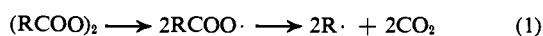
## Polar and Radical Paths in the Decomposition of Diacyl Peroxides<sup>1</sup>

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**Abstract:** The effect of solvents has been determined on the rates and products of decomposition of several diacyl peroxides, which decompose rapidly by presumed concerted scission of two bonds to yield a mixture of "polar" and "radical" products. Decomposition rates increase markedly in going from cyclohexane to acetonitrile, and the increase is accompanied by smaller decreases and increases respectively in yields of radicals scavenged by galvinoxyl and in polar products (including, in acetonitrile amides and imides from attack on solvent). On the basis of these results and literature data it is proposed that in these systems all products arise *via* a single rate-determining transition state, and product distributions are determined by the partitioning of a subsequent intimate ion pair-radical pair. The same formulation is suggested for a variety of cases of molecule-induced homolyses, anchimerically assisted homolyses, and radical rearrangements which show large polar effects and frequently strong solvent dependence.

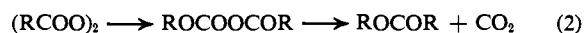
When induced chain processes are eliminated, diacyl peroxides (RCOO)<sub>2</sub>, R = phenyl or primary alkyl) decompose thermally by simple bond homolysis at similar rates which are almost solvent independent. Although there are kinetic complications due to



cage recombination of the primary fragments,<sup>3,4</sup> the chief differences lie in the rate of the second step,  $\beta$  scission to yield R· and CO<sub>2</sub>.<sup>5</sup>

In contrast, peroxides in which R is a secondary or tertiary alkyl or a resonance-stabilized fragment such as benzyl decompose much more rapidly,<sup>6,7</sup> presumably

by a concerted process involving breakage of two or more bonds. Further, rates are now often highly solvent dependent and increase with solvent polarity.<sup>8</sup> It was early noted that such peroxides give relatively high yields of ester in which the stereochemistry of the alkyl portion is conserved.<sup>9,10</sup> More recently several groups<sup>11,12</sup> have shown that the ester is not a primary product, but arises from decomposition of an acyl carbonic anhydride, the "carboxyl inversion product" (eq 2). Such carboxyl inversion products



were first detected in highly asymmetric peroxides<sup>13</sup> and are generally considered to be the consequences of typical electron-deficient rearrangements.

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