

the conversions were 48,400 and 500 dpm, respectively. For the analysis of the products the reaction mixture was treated with alkaline phosphatase and the radioactive alcohols were extracted with light petroleum. Reference terpene alcohols were added to the extract, and it was subjected to radiogas chromatography. The gas chromatography<sup>6</sup> was carried out at a linear programmed temperature at a rate of 4°/min from 140 to 245° on a 1-m PEG 20M column. Helium gas was used as a carrier at a rate of 30 ml/min. In this condition linalool, dihydrogeraniol, geraniol, dihydronerolidol, nerolidol, *trans,trans*-dihydrofarnesol, *trans,trans*-farnesol, *all-trans*-geranylinalool, and *all-trans*-geranylgeraniol had retention times of 3.3, 5.4, 7.0, 8.8, 10.4, 14.2, 16.2, 20.4, and 26.0 min, respectively. Radioactive peaks due to trishomogeraniol and trishomofarnesol derived from 1a appeared at retention times of 11.5 and 21.0 min, respectively, the ratio of the intensities being 4:5. The analysis of the products from 4 also showed two components with retention times of 12.3 and 22.0 min in a ratio of 1:2. Comparison of these retention times with those for the reference prenols and their analogs indicates that these two components correspond to the C<sub>13</sub> and C<sub>18</sub> compounds. The radiogas chromatography on the sample obtained from the acid-treated mixture gave two major radioactive peaks at 7.1 and 16.1 min and two minor peaks at 12.3 and 22.0 min, the former two being attributable to the tertiary alcohols formed by the allylic rearrangement during the hydrolysis. The ratio of the two peaks at 7.1 and 16.1 min was also *ca.* 1:2. These results indicate that the introduction of the Δ<sup>6(7)</sup> double bond has no effect on the termination of the chain elongation, but in the products derived from 4 the C<sub>18</sub> compound was predominant over the C<sub>13</sub> compound, suggesting that the C<sub>13</sub> compound is highly reactive.

The products thus formed by the condensation of 4 with isopentenyl pyrophosphate are nor derivatives 5 and 6 of farnesyl and geranylgeranyl pyrophosphate in regard to the number and position of the double bonds. Liver farnesyl pyrophosphate synthetase, which can synthesize from its natural substrates only farnesyl pyrophosphate,<sup>2</sup> might have also been able to produce geranylgeranyl pyrophosphate if its binding site had been larger than it apparently is, by a space sufficient to accommodate a further *gem*-dimethyl group. Comparison of farnesyl pyrophosphate synthetase and geranylgeranyl pyrophosphate synthetase in this respect would be interesting.

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(6) A Shimadzu Radiogas chromatograph RID 2E was used.

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## The Photolysis of Unsymmetric Azo Compounds

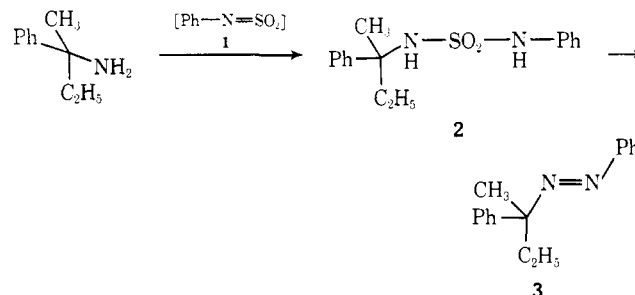
Sir:

Although symmetric azo compounds apparently decompose thermally by simultaneous scission of both

C-N bonds,<sup>1</sup> recent evidence indicates that some unsymmetric azo compounds undergo thermolysis by one-bond cleavage leading to a nitrogen-containing radical.<sup>2,3</sup>

We present here evidence concerning the mechanism of the photoinduced decomposition of a new unsymmetric azo compound, 3. Our observations suggest that 3 undergoes photolysis by an initial one-bond scission. We present new evidence supporting the existence of a nitrogen-containing radical intermediate.

The azo compound 3 was synthesized by the route outlined below.



The unsymmetric sulfamide 2 was prepared by trapping sulfurylaniline 1 (prepared *in situ* from the triethylammonium salt of *N-p*-nitrobenzenesulfonylsulfonamide) with 2-phenyl-2-butylamine.<sup>4</sup> 2 was converted to 3 with NaOH and NaOCl at 45°.<sup>5</sup> The structure of 3 is supported by elemental analysis (*Anal.* Calcd: C, 80.63; H, 7.61; N, 11.75. Found: C, 80.59; H, 7.69; N, 11.89) and uv ( $\lambda_{\max}$  416 nm ( $\epsilon$ 121)), ir, and nmr spectral data. Optically active 3 was obtained if the starting amine had been previously resolved with 1-malic acid.<sup>6</sup> Thus, (-)-2-phenyl-2-butylamine ( $[\alpha]_D -12.2^\circ$  (*c* 8.78, methanol))<sup>7</sup> gave 3 with  $[\alpha]_{389} +82^\circ$ ,  $[\alpha]_{452} +336^\circ$ ,  $[\alpha]_{380} -153^\circ$  (*c* 0.14, octane); CD  $\lambda([\theta]_{\max})$  416 nm,  $\Delta\epsilon +0.34$  (*c* 0.14, octane).

The following observations are important for a discussion of the mechanism of the photolysis of 3: (1) racemization of optically active 3 accompanies photodecomposition; (2) quantum yields for disappearance of 3 are dependent on solvent viscosity; (3) *cis*-3 can be isolated after low-temperature photolysis of *trans*-3.

Thus, 0.01 *M* (+)-3 ( $[\alpha]_{452} +336^\circ$ ,  $[\alpha]_D +82^\circ$ ;  $\Delta\epsilon +0.34$ ) in hexadecane was photolyzed at 25° to 40% completion and the remaining azo compound was recovered and purified by chromatography on alumina.<sup>8</sup> Recovered 3 had  $[\alpha]_{452} +253^\circ$ ,  $[\alpha]_D +61^\circ$ ,  $\Delta\epsilon +0.25$ , indicating optical activity about 74% that of the starting azo compound.<sup>9</sup>

Quantum yields for disappearance of 3 in four solvents are presented in Table I. Samples were irradiated simultaneously on a merry-go-round apparatus

(1) (a) S. Seltzer, *J. Amer. Chem. Soc.*, **83**, 2625 (1961); (b) S. Seltzer, *ibid.*, **85**, 14 (1963).

(2) (a) W. A. Pryor and K. Smith, *ibid.*, **92**, 5403 (1970); (b) W. A. Pryor and K. Smith, *ibid.*, **89**, 1741 (1967).

(3) S. Seltzer and F. T. Dunne, *ibid.*, **87**, 2628 (1965).

(4) W. Lwowski and E. Scheiffle, *ibid.*, **87**, 4359 (1965).

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

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

(7) Amine used for all experiments reported was 67% optically pure.

(8) Thin-layer, ir, uv, and nmr data showed that the recovered 3 was uncontaminated. Control experiments show that the work-up does not lead to any racemization of 3.

(9) Identical results were obtained with more dilute solutions of 3.

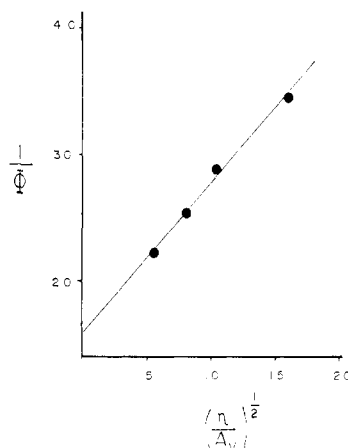


Figure 1. Plot of  $1/\Phi$  vs.  $(\eta/A_v)^{1/2}$  for photodecomposition of **3** at  $25^\circ$  in hydrocarbon solvents.

Table I. Quantum Yields for Disappearance of **3** at  $25^\circ$  <sup>a-d</sup>

Solvent	$\Phi$
Octane	0.044
Decane	0.039
Dodecane	0.035
Hexadecane	0.029

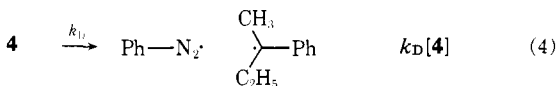
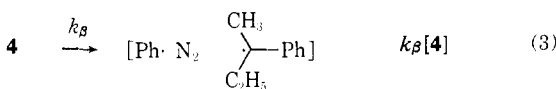
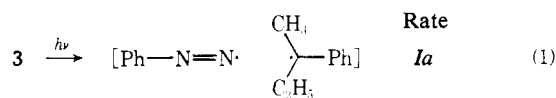
<sup>a</sup> Ferrioxalate actinometer was used. <sup>b</sup> **3** was 0.03 M and absorbed over 99% of the light throughout photolysis. <sup>c</sup> Tubes were let stand in the dark for 2 hr after photolysis and then diluted 1:5, and the remaining **3** analyzed by uv. <sup>d</sup> Samples were sealed under vacuum in matched tubes after degassing three times.

with 436-nm light. Data presented are an average of three experiments.

Photolysis of **3** in pentane at  $0^\circ$  gave some decomposition as well as the *cis* photoisomer of **3**. *cis*-**3** had  $\lambda_{\max}$  shifted to 435 nm. It was much more polar than *trans*-**3** on thin-layer plates and it could be purified by low-temperature column chromatography.<sup>10</sup> *cis*-**3** was stable in the dark at  $-20^\circ$  but it decomposed at  $25^\circ$  with a first-order rate constant of  $k = 1.0 \times 10^{-3} \text{ sec}^{-1}$ . *trans*-**3** as well as decomposition products could be recovered from the thermal decomposition of *cis*-**3**.

The following scheme, similar to the one proposed by Pryor for thermolysis,<sup>2</sup> is useful for the discussion of our results, where  $a$  represents the efficiency of radical-pair production.

Steps 1 and 2 explain the fact that racemization of **3** accompanies decomposition. A bond to the asymmet-



(10) The nmr of the *cis* compound was essentially the same as that of the *trans* with the exception that the signals of the  $-\text{CH}_3$  group and  $-\text{CH}_2-$  methylene of the ethyl group were shifted downfield 6 Hz.

ric carbon is broken in step 1 and internal return (step 2) may lead to racemized **3**. Step 1 is certainly more complex than the simple pathway outlined above. One possible route for decomposition of **3** involves photoisomerization of *trans*-**3** to *cis*-**3** followed by thermal decomposition of the unstable *cis* isomer.<sup>11</sup> We cannot rule out, however, the possibility of a direct photochemical conversion from *trans*-**3** to the radical pair. Our evidence supports the intermediacy of the radical pair **4** and only suggests that *cis*-**3** is involved in one pathway leading to **4**. Kodama<sup>12</sup> has also suggested a one-bond cleavage mechanism for photolysis of symmetric azo alkanes in solution. It would appear, however, that Kodama's observations are inconsistent with such a mechanism.<sup>13</sup>

An expression for the quantum yield for decomposition of **3** can be derived from eq 1-4

$$\Phi = \frac{a(k_D + k_\beta)}{k_D + k_\beta + k_{-1}} \quad (5)$$

Assuming that step 4 is the only process outlined which is viscosity dependent, and that  $k_\beta$  is small compared to  $k_{-1}$  and  $k_D$ , Pryor<sup>14</sup> has shown that

$$\frac{1}{\Phi} = \frac{1}{a} + K \left( \frac{\eta}{A_v} \right)^{1/2} \quad (6)$$

where  $\eta$  is the viscosity and  $A_v$  is the preexponential factor of the Andrade viscosity equation.<sup>15</sup>  $1/\Phi$  vs.  $(\eta/A_v)^{1/2}$  is shown in Figure 1 for the four hydrocarbon solvents.  $a$ , the efficiency of radical-pair production, is calculated to be 0.062 from the intercept.

$f_r$ , the fraction of radicals recombining to yield **3**, can be calculated from eq 7.  $f_r$  calculated in this way

$$f_r = 1 - \frac{\Phi}{a} \quad (7)$$

varies as expected<sup>16</sup> from 0.29 in octane to 0.52 in hexadecane.

We conclude that a one-bond scission-internal return mechanism is operating. We cannot conclude, however, that the production of radicals proceeds solely through thermal decomposition of a *cis*-**3** intermediate. Work on this aspect of the problem is in progress.

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(11) T. Mill and R. Stringham, *Tetrahedron Lett.*, 1853 (1969).

(12) (a) S. Kodama, *Bull. Chem. Soc. Jap.*, **35**, 658 (1962); (b) S. Kodama, S. Fujita, J. Takeisha, and O. Toyama, *ibid.*, **39**, 1009 (1966).

(13) Kodama proposes a one-bond cleavage mechanism on the basis of the temperature dependence of the quantum yield. A variation of 60% (*n*-hexane to *n*-octane) in the viscosity of the solvent resulted in no change in the quantum yield for decomposition, however.

(14) The derivation is the same as that presented in ref 2a for thermolysis.

(15)  $\eta = A_v e^{E/RT}$

(16) See, for example, F. E. Herkes, J. Friedman, and P. D. Bartlett, *Int. J. Chem. Kinet.*, **1**, 193 (1969).

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