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# Thermal and Photolytic Decompositions of Azobis(2-phenylthio)-2-propane

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Thermal and photolytic decompositions of azobis(2-phenylthio)-2-propane have been studied. The reaction mechanisms have been discussed on the basis of products. Almost all reactions of 2-phenylthioprop-2-yl radicals produced from the azo compound photolytically proceed with in-cage processes. The ratio, disproportionation/dimerization, predicts qualitatively that the radical center of the free radical is more electronegative than that of the corresponding oxygen analog.

In a study on the effect of a heteroatom on a radical center, we reported preliminary results on the rates of decomposition of azo compounds that have sulfur or oxygen atoms at α-positions.[1] We consider it worthwhile studying the reactions of free radicals produced from the azo compounds, since this will help to shed light on the nature of the interaction between a heteroatom and a radical center. The photolyses of azo compounds are often used as potential sources of free radicals, but their secondary reaction products have been scarcely studied.

The present study was carried out to see what information the product distribution would give on the mechanism of decomposition of azo compounds. In this paper, we wish to report thermal and photochemical reactions of 2-phenylthioprop-2-yl (**1**) and discuss the mechanism.

$$PhS-\dot{C}(CH_3)_2$$

**1**

## Results

When a 0.25 M solution of azobis(2-phenylthio)-2-propane (**2**) in *p*-xylene was subjected to thermolysis, **2** decomposed completely over a period of 20 hr at 160°C. Products identified from the reaction mixture were 2-phenylthiopropane (**3**), 2-phenylthiopropene (**4**), 2,3-diphenylthio-2,3-dimethylbutane (**5**), diphenyl disulfide (**6**), 2-phenylthio-2-*p*-methylbenzylpropane (**7**), and 4,4′-dimethylbibenzyl (**8**) along with two minor unidentified compounds and polymeric material. On the other hand, the photolysis of the same solution in a pyrex flask at 25°C for 6 hr with the light from a 400 W high-pressure mercury lamp (principal wavelength, 3150 and 3660 Å) led to the complete decomposition of **2** and afforded 2,2-diphenylthiopropane (**9**), propylene (**10**), and 1,2-diphenylthiopropane (**11**) in addition to **3**, **4**, **5**, and polymeric material. Reaction conditions and yields are summarized in Table 1. The results of photolysis of azobis(2-benzyl)-2-propane, a methylene analog of **2**, in benzene are listed in Table 2 for comparison.

Yields were based on the free radical, two species of which had been produced from one molecule of the azo compound, and were determined by combination of vpc and NMR. As **5** and **14** could not be detected by vpc and their NMR spectra are quite similar to those of parent azo compounds, the yields of these compounds were determined by isolation from column chromatograms. For the analyses of gaseous products, mass spectroscopy and vpc were employed.

The free radical **1** can be generated by an alterna-

1) A. Ohno and Y. Ohnishi, *Tetrahedron Lett.*, **1969**, 4405.

Table 1. Products from thermolysis and photolysis of **1** in various conditions

| Run | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|
| Mode of Decomposition | | hν | hν | hν | hν | hν | hν | hν | Δ | Δ |
| Temperature, °C | | 25 | 25 | 25 | 80 | 120 | 160 | 160 | 120 | 160 |
| Time, hr | | 6 | 15 | 40 | 20 | 15 | 10 | 20 | 40 | 20 |
| Product | | | | | | Yield, % | | | | |
| $PhSCH(CH_3)_2$ | **3** | 35.2 | 33.2 | 31.4 | 34.1 | 37.9 | 34.5 | 38.0 | 29.8 | 27.5 |
| $PhSC(CH_3)=CH_2$ | **4** | 14.2 | 9.9 | 5.9 | 7.8 | 7.5 | 7.3 | 6.9 | 3.6 | 8.5 |
| $[PhSC(CH_3)_2]_2$ | **5** | + | + | 13.0[a] | + | + | + | + | + | 9.0[a] |
| PhSSPh | **6** | ..... | ..... | Trace | ..... | ..... | 2.6 | 4.0 | 3.9 | 6.5 |
| $PhSCMe_2CH_2C_6H_4CH_3$-*p* | **7** | 0 | 0 | 0 | Trace | 0.8 | 5.2 | 5.5 | 5.7 | 7.8 |
| $(PhS)_2C(CH_3)_2$ | **9** | 7.8 | 10.3 | 12.4 | 8.7 | 3.8 | 4.7 | 3.9 | 0 | 0 |
| $CH_3CH=CH_2$ | **10**[b] | + | + | + | + | + | + | + | 0 | 0 |
| $PhSCHMeCH_2SPh$ | **11** | 1.9 | 3.4 | 4.6 | + | + | + | + | Trace | Trace |

a) Isolated yields. b) Qualitatively analyzed.

Table 2. Products from photolysis of azobis-(2-benzyl)-2-propane in benzene at 25°C

| Product | | Yield, % |
|---|---|---|
| $PhCH_2CH(CH_3)_2$ | **12** | 50.7 |
| $PhCH_2C(CH_3)=CH_2$ | **13** | 37.8 |
| $[PhCH_2C(CH_3)_2]_2$ | **14** | 11.5 |

Table 3. Products from photolysis of a mixture of **3** and DTBP at 25°C

| Product | | Yield, %[a] |
|---|---|---|
| $PhSC(CH_3)=CH_2$ | **4** | Trace |
| $PhS(CH_2)_2CH_3$ | **15** | 3.5 |
| PhSSPh | **6** | 9.7 |
| $CH_3CH=CH_2$ | **10**[b] | + |
| $(PhS)_2C(CH_3)_2$ | **9** | Trace |

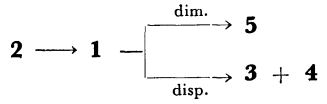
a) DTBP : **3** = 1 : 1 in mol ratio. Conversion = 11.6%
b) Qualitatively analyzed.

tive method. A mixture of **3** and di-*t*-butylperoxide (DTBP) (1 : 1 in mole ratio) was irradiated in the same way as described above, which resulted in no products expected from bimolecular reactions of **1** (except for trace of **4**) being found (see Table 3). Instead, a considerable amount of **6** and **10** with a small amount of phenyl *n*-propyl sulfide (**15**) were isolated.

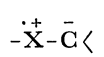
## Discussion

The products could be divided into several groups according to the reactions for their formation, *via*, disproportionation, dimerization and hydrogen abstraction of **1**. The former two proceed by either thermal or photolytic conditions, while hydrogen abstraction takes place only at elevated temperatures. All the reactions give important information and it will be convenient to discuss them separately.

*Disproportionation and Dimerization.* The presence of **3**, **4**, and **5** in the reaction mixture invokes unequivocally that both thermal and photolytic decompositions of **2** proceed with a radical mechanism.




Although yields of disproportionation products **3** and **4** are not counterbalanced, this is mainly due to their further decomposition or polymerization. As seen in Table 1, the longer the reaction time and the higher the temperature, the lower their yields, It is apparent that disproportionation is not the only route to **3** at least for thermolysis (*vide infra*). for This also seems true for photolysis, because the yields of **12** and **13** are unbalanced in spite of the fact that 100% of products have been identified. It is noteworthy that the ratio of yields, (**3**+**4**)/**5** or disproportionation/dimerization, is considerably smaller than the corresponding values with the methylene and oxygen analogs.[2] These ratios do not represent exactly the relative ratios of disproportionations and dimerizations. However, this tendecy indicates, at least qualitatively, that the electron density at the radical center decreases by a substituent at an α-position with the order $O \gg CH_2 \gtrsim S$.[3-5] This seems to imply that a canonical form **16** is more important for the oxygen analog than for the sulfur one.[1]



**16**

The photolytic decomposition of **2** produces almost all these compounds by "in-cage" reactions, since the reaction of **3** with DTBP does not afford them in a measurable amount. In the latter reaction, **1** is not paired by a partner and has difficulty in encountering one.

2) A. Ohno, N. Kito, and Y. Ohnishi, This Bulletin, **44**, 467 (1971).
3) S. W. Benson, *Advan. Photochem.*, **2**, 1 (1964).
4) a) J. R. Shelton, C. K. Liang, and P. Kovacic, *J. Amer. Chem. Soc.*, **90**, 354 (1968); b) P. Kovacic, R. R. Flynn, J. F. Gormish, A. H. Kappelman, and J. R. Shelton, *J. Org. Chem.*, **34**, 3312 (1969).
5) P. J. Wagner and H. N. Schott, *J. Amer. Chem. Soc.*, **91**, 5383 (1969).

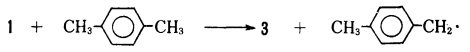
Another interesting phenomenon, seen in Table 2, is that the olefin formed by disproportionation was only **13** and no **17** was detected, contrary to expecta-

$$PhCH=C(CH_3)_2$$

**17**

tion from the reactivities of hydrogen.[6] There are few such examples of high selectivity in radical reactions. Steric effects seem to play an important role for hydrogen abstraction.[7]

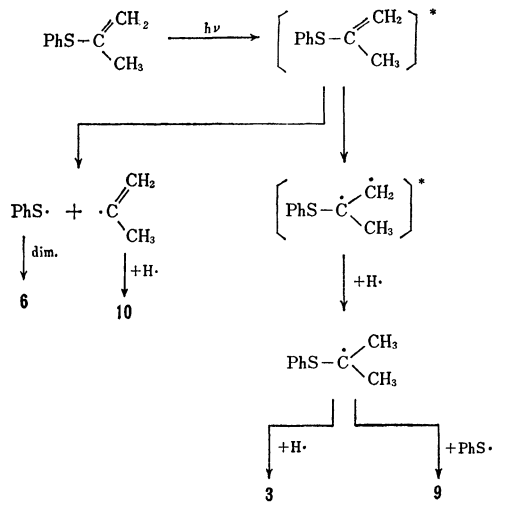
*Hydrogen Abstraction from the Solvent.* Since **7** and **8** are formed only at elevated temperatures, the



reaction might require a certain amount of activation energy. Taking into account the lifetime of **1**,[8] it is reasonable to attribute a "cage-wall" reaction for the formation of **7**.

*Photochemical Reactions.* Formation of **9** and **10** presents an interesting photochemistry. Since these compounds are not afforded by thermal reactions (runs 8 and 9 in Table 1) and since the experiment shown in run 7 in Table 1 confirms that they are not consumed by further reactions under the present thermal conditions, it is apparent that these compounds have been formed by a photochemical process.

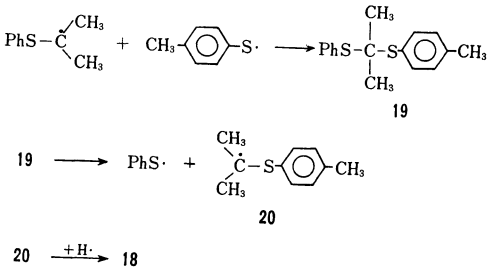
A control experiment revealed that they were formed from olefin, **4**, photochemically. The increase of the yield of **9** with prolonged irradiation (runs 1 to 3 in Table 1 and Experimental) can be attributed to this reaction. The mechanism may be as follows.



The olefin is known to undergo photocyclization yielding a benzothiophene derivative.[9] However, this mode of photodissociation has not been reported. It is interesting to note the formation of a vinyl radical.

Although **11** is formally afforded by the addition of thiophenol to **4**, there is an alternative pathway: the migration of **9** to **11**.[10,11] However, a control experiment showed that such a reaction does not take place under the present conditions both photochemically and thermally.

We claimed thermal carbene-formation from the fact that thermolysis of **2** in *p*-tolylmercaptan affords *p*-tolyl isopropyl sulfide (**18**).[1] However, we now believe that the mechanism of this reaction can be better ascribed to the addition-elimination process:



When a solution of **9** in *p*-tolylmercaptan was kept at 160°C for 20 hr, 2,2-(*p*-tolylthio)propane was isolated in good yield.

## Experimental

*Materials.* Azobis(2-phenylthio)-2-propane (**2**) was prepared according to Benzing[12]; mp 90—90.5°C (lit, 90—90.5°C).

Azobis(2-benzyl)-2-propane was synthesized by the oxidation of 1,1-dimethyl-2-phenylethyl amine with $IF_5$;[13] 120 m*l* of $CH_2Cl_2$, 18 m*l* of pyridine, and more than 5 m*l* of $IF_5$ were placed in a 1*l* three-necked flask equipped with a mechanical stirrer, a dropping funnel, and a refluxing condenser, and cooled to about −10°C with a dry ice—$CCl_4$ bath. A solution of 1,1-dimethyl-2-phenylethyl amine (14 g)[14] in $CH_2Cl_2$ (10 m*l*) was then added slowly through dropping funnel. The whole mixture was stirred further for 1 hr at −10°C and 2 hr at 0°C. After excess $IF_5$ had been decomposed with water, the organic layer was washed with water, dilute aq-HCl, and 5% aq-$Na_2S_2O_3$, and dried over Drierite. Evaporation of the solvent under reduced pressure left a dark-brown oil, which was extracted with ether giving crystalline material. Recrystallization from methanol gave 2.5 g of the azo compound (mp 68—70°C).

Found: C, 81.70; H, 8.98; N, 9.61%. Calcd for $C_{20}H_{26}N_2$: C, 81.58; H, 8.90; N, 9.52%.

Authentic samples were prepared according to refer-

6) W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., New York, N. Y. (1966), pp. 149—175.

7) W. D. Totherow and G. J. Gleicher, *J. Amer. Chem. Soc.*, **91**, 7150 (1969).

8) A. Ohno, N. Kito, and Y. Ohnishi, This Bulletin, **44**, 470 (1971). The ESR signal could not be obtained by photolysis of **2** at room temperature, though its oxygen and methylene analogs gave signals. This fact indicates that the lifetime of **1** is fairly short, which is also evidenced by the distribution of products from the reaction of **3** with DTBP.

9) S. H. Groen, R. M. Kellogg, J. Buter, and H. Wynberg, *J. Org. Chem.*, **33**, 2218 (1968).

10) R. Kh. Freidlina, A. B. Terent'ev, and R. G. Petrova, *Dokl, Akad. Nauk SSSR*, **149**, 860 (1963); *Chem. Abstr.* **59**, 7411b (1963).

11) R. Kh. Freidlina, *Advan. Free-Radical Chem.*, **1**, 211 (1965).

12) E. Benzing, *Ann. Chem.*, **631**, 1 (1960).

13) S. F. Nelsen and P. D. Bartlett, *J. Amer. Chem. Soc.*, **88**, 137 (1966); T. E. Stevens, *J. Org. Chem.*, **26**, 2531 (1961).

14) J. J. Ritter and J. Kalish, *J. Amer. Chem. Soc.*, **70**, 4048 (1948).

ences.[15-19]

*Photolysis. General Procedure*: Unless otherwise indicated, all photolyses were carried out in pyrex tubes (15 mm o.d.) using a 400 W high-pressure mercury lamp (Riko-Kagaku Sangyo), which was placed in a water-cooled quartz immersion well.

All the solutions (0.25 M in purified *p*-xylene) were degassed under reduced pressure at $10^{-4}$ mmHg by the freeze-thaw method to exclude air and oxygen, and then were sealed in the usual manner. Sample tubes were placed 40 mm from the source of light.

Photolyses at elevated temperatures were performed by using a two-necked quartz tube; a sample tube was inserted from one side with the thermometer and hot air was introduced from the other. Temperatures were maintained within ±3°C.

*Photolysis of* ***2***: Run 3 of Table 1 will be described in detail as a typical example. Photolysis of **2** (825 mg) was performed at 25°C for 40 hr. Compounds **3** and **4** were identified by retention time with those of authentic samples on vpc and by IR and NMR spectra. After elimination of excess solvent, **3**, and **4** under reduced pressure, the concentrated mixture was chromatographed on a column of silica gel (200 mesh) packed in petroleum ether. Elution of the column with a mixture of petroleum ether and benzene (90 : 10) yielded 98 mg (13%) of **5**, a trace of **6**, and an oil. Compound **5** was recrystallized from ethanol, mp 126—127°C, whose NMR spectrum had signals at ($\delta$ from TMS in $CCl_4$) 1.41 (s, 12H) and 7.02—7.35 (m, 10H).

Found: C, 71.27; H, 7.32; S, 21.07%. Calcd for $C_{18}H_{22}S_2$: C, 71.50; H, 7.33; S, 21.17%.

An oil was rechromatographed on a column of silica gel with petroleum ether - benzene (85 : 15) mixture as an eluent. Purified oil was identified to be **9** by comparing IR, NMR and mass spectra with those of the authentic sample as well as elemental analyses. Compound **11** was also obtained as an oil on column chromatographic separation on silica gel, IR, NMR, and mass spectra of which were identical with those of the authentic compound.

Formation of **10** was carefully examined by an independent photolysis of **2** in a breakable-sealed tube. Gas analyses on mass spectrometry and gas chromatography showed the presence of **10** in a considerable amount.

*Thermolysis. General Procedure*: Aliquots prepared as described above were placed in an oil bath of 160°C. Temperature was maintained within ±1°C.

*Thermolysis of* ***2***: Run 9 of Table 1 will be described in detail as a typical example. Thermolysis of **2** (825 mg) was undertaken at 160°C for 20 hr. After the decomposition of **2** had been completed, **3**, **4**, and **6** were analyzed by VPC quantitatively. The reaction mixture was chromatographed on a column of silica gel packed in petroleum ether after the elimination of the solvent and **3** under reduced pressure. Elution of the column with a mixture of petroleum ether and benzene (90 : 10) gave white crystals and **6**. The crystals were identified to be **7** by the following evidence: NMR ($\delta$ from TMS in $CCl_4$) 1.15 (s, 6H), 2.28 (s, 3H), 2.76(s, 2H), 6.94(s, 4H), and 7.08—7.60 (m, 5H). Mass spectrum showed a parent peak at *m/e* 256 and a base peak at *m/e* 151 $(PhSCMe_2)^+$.

Found: C, 79.79; H, 7.87; S, 12.51%. Calcd for $C_{17}H_{20}S$: C, 79.65; H, 7.86; S, 12.48%.

Compound **8** was collected by vpc and was rechromatographed on a column of silica gel and its identity was confirmed with the authentic compound.

The presence of **10** in a mixture of thermolysis products was examined independently. There was no indication of the formation of this compound.

*Thermolysis and Photolysis of* ***3***. Thermolysis (160°C) and photolysis (25°C) of **3** in *p*-xylene (0.25 M) were carried out in degassed tubes for 20 hr. It was found that no reaction had taken place.

*Photolysis of* ***4***. A solution of **4** in *p*-xylene was irradiated as described above. Reaction conditions and results are summarized in Table 4.

TABLE 4. PRODUCTS FROM PHOTOLYSIS OF **4** IN *p*-XYLENE AT 25°C

| Irrad. Time, hr | | 20 | 40 |
|---|---|---|---|
| Conversion, % | | 62.1 | 89.0 |
| Product | | Yield, %[a] | |
| $PhSCH(CH_3)_2$ | **3** | Trace | Trace |
| PhSSPh | **6** | 6.5 | 5.9 |
| $CH_3CH{=}CH_2$ | **10**[b] | + | + |
| $(PhS)_2C(CH_3)_2$ | **9**[c] | 16.2 | 11.5 |

a) Based on consumed **4**. b) Qualitatively analyzed. c) Contaminated by a trace of **11**.

*Thermal and Photochemical Additions of Thiophenol to* ***4***. Equimolar mixtures of thiophenol and **4** in benzene (4.0 ml, 0.25 M) and in *p*-xylene (4.0 ml, 0.25 M) were subjected to photochemical (25°C) and thermal (160°C) reactions, respectively. No quantitative analysis on products was carried out. However, anti-Markownikoff addition product **11** was obtained, along with **6** and unreacted **4**, from both reactions.

*Thermal and Photochemical Rearrangements of* ***9***. Thermolysis (160°C) and photolysis (25°C) of **9** in *p*-xylene (5.0 ml, 0.5 M) were performed in evacuated sealed tubes for 20 hr. Most of the starting material was recovered along with small amounts of **6**, **4**, and an unidentified material. It is apparent that the thermal and photochemical rearrangements from **9** to **11** did not occur. No formation of **10** took place.

*Thermal Decomposition of* ***5***. Compound **5** (148 mg) was thermally decomposed in *p*-xylene (2.0 ml) at 160°C for 20 hr. Most of **5** was found to be recovered, but was detected the formation of 2,3-dimethylbutene-2 by vpc and mass spectrometry along with **6**.

*Thermal and Photochemical Decompositions of* ***11***. Thermolysis (160°C, 40 hr) and photolysis (25°C, 40 hr) in *p*-xylene (5.0 ml, 0.25 M) were carried out in a degassed sealed tube. No definite change took place in both reactions. Original **11** was mostly recovered. Propylene **10** was detected by analyses of gaseous products.

*The Reaction of* ***3*** *with DTBP*. An equimolar mixture of **3** and DTBP was degassed thoroughly and sealed in a pyrex tube. Photoirradiation was carried out at 25°C for 20 hr. Product analysis was carried out as described before. Compound **12** was collected by vpc and was rechromatographed on a column of silica gel. Identity of its structure with that of the authentic compound was confirmed by

15) $PhSCH(CH_3)_2$, bp 110.5—111.5°C/40 mmHg (lit, 260.5—207.5°C): V. N. Ipatieff, H. Pines, and B. S. Friedman, *J. Amer. Chem. Soc.*, **60**, 2731 (1938).

16) $PhSC(CH_3){=}CH_2$, bp 79—84°C/10 mmHg (lit, 97—98°C/20 mmHg): W. H. Muller and K. Griesbaum, *J. Org. Chem.*, **32**, 856 (1967).

17) $(CH_3)_2C(SPh)_2$, bp 162°C/0.25 mmHg (lit, 146°C/0.1 mmHg): A. Schonberg and K. Praefcke, *Chem. Ber.*, **100**, 778 (1967).

18) $PhSCH(CH_3)(CH_2SPh)$, 176—179°C/4 mmHg (lit, 166—167°C/2 mmHg): Ref. 11.

19) $PhCH{=}C(CH_3)_2$, collected by vpc: R. N. Castle and C. F. Poe, *J. Amer. Chem. Soc.*, **66**, 1438 (1944).

spectral data.

*The Reaction of* **9** *with* p-*Tolylmercaptan.* In a degassed and sealed tube, 0.1303 g ($5\times10^{-4}$ M) of **9** and 5.0 g ($4\times10^{-2}$ M) of *p*-tolylmercaptan were placed. The mixture was kept at 160°C for 20 hr. Excess *p*-tolylmercaptan was eliminated from a reaction mixture under reduced pressure, bp 72—74°C/12 mmHg. The residue was chromatographed on silica gel with petroleum ether-benzene (90 : 10) mixture as an eluent, yielding 0.133 g (92%) of 2,2-(*p*-tolylthio)propane: mp 65—66°C (lit,[20] mp 66°C).

We wish to thank Dr. G. Tsuchihashi of Sagami Chemical Research Center for useful discussion.

20) E. Fromm and G. Raiziss, *Ann. Chem.*, **374**, 90 (1910).