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Thermal and Photolytic Decompositions of Azobis(2-phenoxy)-2-propane

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Thermal and photolytic decompositions of azobis(2-phenoxy)-2-propane have been studied. More than half of the 2-phenoxyprop-2-yl radicals thus produced thermally cause the phenyl group to migrate from oxygen to the carbon, followed by elimination of the methyl group. Most of the remaining radicals abstract hydrogen from the solvent. When phenyl ether is employed as a solvent, homolytic aromatic substitution takes place yielding isopropylbenzene derivatives. It is shown by mechanistic consideration, although not completely decisively, that this is a new type of reaction in the sense that a part of the leaving group constitutes a part of the entering group.

In contrast to the ionic species, little has been studied on the effect of heteroatoms in free radicals. In a previous paper concerning kinetics of decompositions of azo compounds which have heteroatoms at α-positions, we reported that an α-oxygen atom exerts very minor, if any, effect on the stabilization of a carbon radical in comparison to an α-methylene group, while a sulfur atom stabilizes it extensively.[1] On the other hand, it is known from the study on ESR spectroscopy that a free radical which has an α-oxygen atom has much longer lifetime than its methylene or sulfur analog under the irradiation of light.[2] These facts indicate that the oxygen-containing radical is less reactive than others at least under the condition of photolysis. This prompted us to study the mechanism of thermal and photochemical decompositions of azobis(2-phenoxy)-2-propane (**1**) and of secondary reactions involving 2-phenoxyprop-2-yl (**2**).

$$\mathrm{PhO\text{-}\dot{C}(CH_3)_2}$$

2

This paper deals with the analyses of final products of these reactions. The results are discussed in comparison to those obtained with sulfur and methylene analogs of **2**.[3]

Results

A 0.25 M solution of **1** in *p*-xylene was subjected to thermolysis at 160°C for 20 hr. Identified products were 2-phenoxypropane (**3**), 2-phenoxypropene (**4**), 2,3-diphenoxy-2,3-dimethylbutane (**5**), acetophenone (**6**), and methane (**7**) along with a considerable amount of *p,p'*-dimethylbibenzyl (**8**). Irradiation of light from a 400 W high-pressure mercury lamp to the same solution in a pyrex flask at 25°C for 6 hr (principal wavelength 3150 and 3660 Å) gave **3**, **4**, **5**, and phenol (**9**). Results are summarized in Table 1. Yields were based on the free radical **2**, two species of which had been produced from one molecule of the azo compound, and were determined by using vpc and NMR except for **5**. Since **5** has identical NMR signals to those of **1** and it decomposes in a column of vpc, the yield of this compound was obtained by isolation from a column chromatogram.

Irradiation of light to a mixture of **3** and di-*t*-butylperoxide (DTBP) also affords the same free radical, **2**. Products obtained were **4**, **5**, **9**, and a mixture of

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

Run		1	2	3	4	5
Mode of decomposition		hν	hν	hν	hν	Δ
Temperature, °C		25	25	80	120	160
Time, hr		6	40	20	15	20
Product				Yield, %		
$PhOCH(CH_3)_2$	**3**	39.2	42.2	43.4	38.8	45.1
$PhOC(CH_3){=}CH_2$	**4**	31.8	28.7	24.9	20.1	4.2
$[PhOC(CH_3)_2]_2$	**5**[a]	1.3	1.5	1.1	1.2	Trace
$PhCOCH_3$	**6**	0	0.4	2.7	4.7	50.7
CH_4	**7**[b]	—	—	—	—	+
$[p\text{-}CH_3C_6H_4CH_2]_2$	**8**[c]	Trace	2.1	5.6	10.9	64.0
PhOH	**9**	8.1	8.5	8.6	8.8	0

a) Isolated yields.
b) Qualitatively analyzed.
c) Calculated by assuming the formation of one species of *p*-methylbenzyl radical from one species of **2**.

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

[2] A. Ohno, N. Kito, and Y. Ohnishi, This Bulletin, **44**, 470 (1971).

[3] A. Ohno, N. Kito, and Y. Ohnishi, *ibid.*, **44**, 463 (1971).

isomers of isopropoxycymenes. Since the last mixture consisted of more than 95% of *o*-isomer, we will refer to this as *o*-isopropoxycumene (**10**). The results are listed in Table 2.

Table 2. Products from photolysis of a mixture of **3** and DTBP at 25°C

Mol Ratio (**3**/DTBP)		2	1
Conversion, %		4.0	25.4
Product		Yield, %	
$PhOC(CH_3)=CH_2$	**4**	Trace	24.2
o-Isopropoxycumene	**10**	51.5	7.2
PhOH	**9**	42.5	5.4
$[PhOC(CH_3)_2]_2$	**5**	Trace	12.4

Azobis(*p*-tolyloxy)-2-propane (**11**) was also decomposed in *p*-xylene at 160°C under irradiation of light for 15 hr. Products identified were *p*-methyl derivatives of **3**, **4**, **6**, and **9**. Neither *o*,*o*′-dimer nor *o*,*p*′-dimer of cresol (Pummerer's ketone)⁴⁾ was detected. In isopropoxybenzene, **1**, **11**, and azobis(*p*-chlorophenoxy)-2-propane (**12**) decomposed photolytically. Yields of *o*-isopropoxycumene are listed in Table 3 together with the result of thermolysis of **1** in the same solvent.

Table 3. Yields of *o*-isopropoxycumene

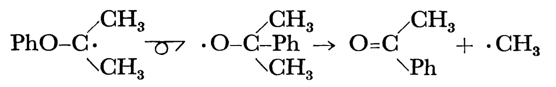
Azo compound	Yield, %	
	$h\nu^{a)}$	$\Delta^{b)}$
1	21.3	19.4
11	1.2	—
12	2.8	—

a) At 25°C. b) At 160°C.

Discussion

In view of the product distribution, marked difference can be seen between thermal and photolytic decompositions of **1**. Acetophenone is formed as a main product of thermolysis, while it is absolutely absent in the photolysis mixture. On the other hand, phenol is produced only by photolysis. Furthermore, as seen in the reaction of **3** with DTBP, homolytic aromatic substitution takes place when a reasonable amount of phenyl ether is present, which is not the case with phenyl sulfides or with aromatic hydrocarbons. These and other observations will be discussed respectively under separate titles.

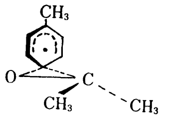
Migration. The presence of acetophenone and methane suggests clearly that the reaction takes place



$$PhO{-}\overset{CH_3}{\underset{CH_3}{C}}\cdot \longrightarrow \cdot O{-}\overset{CH_3}{\underset{CH_3}{C}}{-}Ph \rightarrow O{=}\overset{CH_3}{\underset{Ph}{C}} + \cdot CH_3$$

in the solution. Although this type of rearrangement is known in gas phase,⁵⁻⁷⁾ this is the first example of migration in a solution. The second step of the reaction takes place easily in solution and has been studied both kinetically⁸⁻¹⁰⁾ and spectroscopically.¹¹⁾ Activation energy is estimated to be about 8 kcal/mol.⁸⁾ Cumyloxy radicals generated by the photolysis of dicumyl peroxide in benzene have too short a life for ESR detection at a room temperature.¹¹⁾ However, 2-phenoxyprop-2-yl radicals generated by the photolysis of **1** in *p*-xylene have enough lifetime for detection after the irradiation of light has been stopped.²⁾ From the results, migration seems to require activation energy of more than 8 kcal/mol.

The fact that the same reaction with **11** affords *p*-methylacetophenone solely, seems to suggest that migration proceeds through a transition state expressed by **13**.



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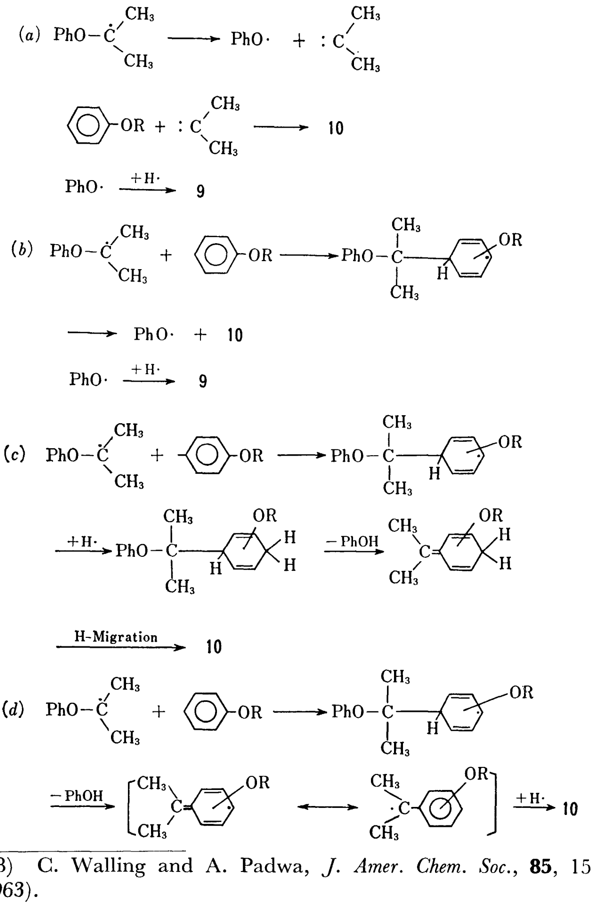
Homolytic Aromatic Substitution. When a mixture of **3** and DTBP is irradiated with light, a large amount of **9** and **10** is formed at the sacrifice of **4**.¹²⁾ The aromatic substitution of the same type also takes place when **1**, **11**, and **12** are decomposed in **3**. Several mechanisms are possible for this substitution:



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where R stands for an isopropyl group and many other canonical forms are neglected for simplicity.

Mechanism *a* is highly implausible, since almost exclusive formation of the *o*-isomer cannot be explained by this mechanism.[13] In addition, there is no indication of carbene-formation during the reaction.[14] On the other hand, the predominancy of *o*-attack is well established in free-radical aromatic substitution.[15]

Although mechanism *b* seems reasonable, it involves free-radical 1,2-hydrogen shift. Despite much effort to find such a type of migration, nothing has been achieved.[16] This reduces the possibility of this mechanism greatly. Furthermore, it is important to consider the formation of phenol. If a phenoxy radical is a precursor of a phenol, we might expect coupling products at least in a detectable amount. However, no such compound was found. This implies that phenol results not from phenoxy radicals but from something which can eliminate it directly. Thus, mechanisms *c* and *d* remain as plausible pathways.

The difference between these mechanisms lies on the timing of hydrogen abstraction. The former mechanism involves abstraction of a hydrogen by a cyclohexadienyl radical before a phenol departs from it. This type of reaction is well known.[17–20] On the other hand, the latter mechanism consists of the elimination of a phenol followed by hydrogen abstraction at a benzyl position. Although it is impossible to decide which mechanism is correct without further information, we believe that mechanism *d* is more plausible than the others. In mechanism *d*, the driving force for the elimination of phenol could be attributed to the aromatization of a cyclohexadienyl radical. No such energy gain can be found in the step of phenol elimination in mechanism *c*.

It is noteworthy that this type of substitution is greatly reduced when **2** has a substituent at the *p*-position (Table 3) and that no reaction takes place when phenyl isopropyl sulfide is employed as a solvent. These facts suggest considerable contribution of electronic effect(s) for this reaction.[21] Even though mechanism *d* is plausible, some variations must be considered in this mechanism to elucidate giving *o*-isomer predominantly.

It should be noted anyhow that the reaction is of a new type of homolytic aromatic substitution in the sense that the entering group itself keeps a part of the leaving group.

Hydrogen Abstraction from the Solvent. The result of run 5 in Table 1 shows that about 40% of **2** thermally produced abstracts hydrogen from the solvent. At lower temperatures, discrepancies of yields of **3** and **4** are much smaller or almost comparable indicating disproportionation is much more important than hydrogen abstraction from the solvent. The corresponding value for the sulfur analog of **2** is at most 15%.[3] Uneyama and co-workers have reported that the relative reactivity of thioanisole and anisole toward hydrogen abstraction by *t*-butoxy radicals is only 1.5 : 1.0.[22] Although the present result is far from quantitative and cannot be compared to kinetic data precisely, longer life of **2** than its sulfur analog seems to play an important role for such a great facility of **2** in hydrogen abstraction. Thus, **2** has many chances to escape from a solvent-cage or from its counterpart and to react with the solvent in "out-of-cage" process. Since the sulfur analog of **2** is short-lived, the only chance for it to react with the solvent is a process of "cage-wall" reaction. According to this scheme, it is understandable why the sulfur analog of **2** affords 2-phenylthio-2-*p*-methylbenzylpropane and **2** does not afford the corresponding oxygen compound: when a *p*-methylbenzyl radical is formed at "cage-wall", as being the case of the sulfur compound, it is easily captured by a radical in "cage", while a *p*-methylbenzyl radical produced at out of "cage" has little chance to find such a counterpart.

Experimental

Materials. Azobis(2-phenoxy)-2-propane (**1**) was prepared after Benzing[23] from the corresponding chloride and phenol. For this reaction, however, ethanol was not a useful solvent and *N,N'*-dimethylformamide was employed (yield, 40%): mp 91—92°C.

Found: C, 72.80; H, 7.40; N, 9.43%. Calcd for $C_{18}H_{22}N_2O_2$: C, 72.45; H, 7.43; N, 9.39%.

Azobis(2-*p*-tolyloxy)-2-propane (**11**) was also prepared with 25% yield as described above: mp 76—78°C.

Found: C, 73.42; H, 8.11; N, 8.73%. Calcd for $C_{20}H_{26}N_2O_2$: C, 73.59; H, 8.03; N, 8.58%.

Azobis(2-*p*-chlorophenoxy)-2-propane (**12**) was prepared with the same procedure: mp 95—96°C.

Found: C, 58.88; H, 5.51; N, 7.82; Cl, 19.31%. Calcd or $C_{18}H_{20}Cl_2N_2O_2$: C, 58.87; H, 5.49; N, 7.63; Cl, 19.31%.

Photolysis and Thermolysis of Azo Compounds. A general procedure has been described previously.[3] All products except for **4** were identified by comparing their IR, NMR, and mass spectra and retention times of vpc with corresponding authentic compounds. Compound **4** was isolated from a column chromatogram of silica gel (200 mesh) and its structure was confirmed by the following data: mp 103—103.5°C. NMR (δ from TMS in CCl_4) 1.42 (s).

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[14] Propylene was isolated from the reaction mixture of the sulfur analog of **2** under the photolytic condition. For detail, see Ref. 2.

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Found: C, 79.77; H, 8.29%. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20%.

The Reaction of **3** *with DTBP.* The procedure and the method of product analyses were the same as described above. Compound **10** was collected by vpc and its NMR spectrum was found to be nearly the same as that of the authentic sample of *o*-isopropoxycumene: bp 93—93.5°C/13.5 mmHg (lit,[24] 223—240°C).

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