[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

The Photolysis of Isobutyl Disulfide in Cumene[1]

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The photolysis of isobutyl disulfide in cumene at 35.0°, using a low pressure mercury arc, results in the rapid formation of isobutyl mercaptan. The initial rate of mercaptan formation is independent of disulfide concentration and, therefore, independent of the fraction of light initially absorbed by the disulfide. This effect is discussed in detail and the conclusion drawn that cumene acts as a photosensitizer for the dissociation of the disulfide. The percentage conversion of disulfide to mercaptan is independent of initial disulfide concentration as well as light intensity. The observation that hydrogen is produced in significant quantities during the photolysis suggests that a steady state is reached in which the rate of formation of mercaptan is equal to the rate of its photochemical destruction. The only other single major product of the reaction, besides isobutyl mercaptan, is 2,3-dimethyl-2,3-diphenylbutane (dicumene) which arises by the dimerization of α,α-dimethylbenzyl radicals. The rest of the products are a complex mixture of sulfides, some having molecular weights of over 400 and containing at least three atoms of sulfur per molecule. Evidence is presented that this mixture arises from a series of disproportionations. A few experiments on other systems also are reported.

Reactions of the type

$$RS\cdot + HR' \longrightarrow RSH + R'\cdot \qquad (1)$$

represent the reverse of the chain transfer step in the free radical addition of thiols to olefins.[3] The RS–H bond dissociation energy of *n*-alkyl mercaptans from electron impact data is approximately 86 kcal.[4] If the C–H bond dissociation energy of benzyl type radicals is assumed to be the same as in toluene, 77.5 kcal.,[5] then one concludes, even taking into account the appreciable error in bond dissociation energies (at least ±2 kcal.), that such reactions, where R′ = benzyl, should be exothermic processes. Further, the calculated endothermicity of the reverse process, 8.5 kcal., is within experimental error of the activation energy for chain transfer of polymerizing styrene with simple mercaptans (~6.5 kcal.) so they should occur with negligible activation energy.[6]

Several scattered observations in the literature support this view. In 1937, Ritter and Sharpe[7] reported that tetralin, refluxed in isoamyl disulfide, yielded naphthalene in 70% yield as well as isoamyl mercaptan. The reaction appeared to go more rapidly in old (peroxide-containing) tetralin. This sort of reaction was reinvestigated by Nakasaki[8] who found a similar dehydrogenation of tetralin, 9,10-dihydroanthracene and phenylcyclohexane by phenyl disulfide and 2-benzothiazyl disulfide at 260°. Presumably at these temperatures some dissociation of the disulfide into radicals occurs. The idea that a radical reaction is involved is supported by the observation that similar reactions may be induced photochemically at room temperature.[9] Thus, ultraviolet irradiation of benzothiazyl disulfide dehydrogenates tetralin, cyclohexene and squalene, and exposure to sunlight of an ether solution of phenyl disulfide and benzhydrol leads to benzopinacol and thiophenol. In 1948, Lyons[10] reported that the photolysis of *o*-tolyl and *p*-tolyl disulfides gives rise to mercaptans, but with low quantum yield (0.046). The mercaptan-catalyzed decarbonylation of aldehydes[11] undoubtedly involves abstraction of the carbonyl hydrogens by thiyl radicals. The formation of the dimer of 9,10-dihydroanthracene when α-phenylazoethane is thermally decomposed at 125° in the presence of *n*-octyl mercaptan and 9,10-dihydroanthracene is accounted for by assuming that *n*-octyl thiyl radicals abstract labile hydrogens from the hydrocarbon.[12] Cohen and Wang[13] observed that the sun lamp irradiation of a dilute solution of phenyl disulfide in diphenylmethane results in a 72% yield of 1,1,2,2-tetraphenylethane.

A preliminary investigation at Columbia[14] of the ultraviolet-catalyzed reaction of 0.26 *M* solutions of *n*-butyl disulfide in several hydrocarbons revealed the following extents of reaction, as measured by thiol yields: cumene, 29%; ethylbenzene, 19%; toluene, 4.5%; 2,2,4-trimethylpentane (isoöctane), 2.5%; and cyclohexane, very small. This is the order expected if one considers the relative C–H bond strengths of the compounds involved. Since only 29% of the theoretical *n*-butyl mercaptan was produced in the photolysis of *n*-butyl disulfide in cumene and only a fraction of the calculated amount of the dimeric 2,2-dimethyl-3,3-diphenylbutane was isolated,[14] a detailed study of the photolysis of disulfides in hydrocarbons was undertaken. The system chosen for both kinetic study and careful product analysis was isobutyl disulfide–cumene at 35.0°.

Results and Discussion

Kinetic Study of the Irradiation of Isobutyl Disulfide in Cumene.—The irradiation of isobutyl disulfide in cumene at 35.0° produces isobutyl mercaptan quite readily, presumably by the attack of a

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[2] University Fellow in Chemistry, 1956–1957.

[3] M. S. Kharasch, A. T. Read and F. R. Mayo, *Chemistry & Industry*, **57**, 752 (1938).

[4] J. L. Franklin and H. E. Lumpkin, THIS JOURNAL, **74**, 1023 (1952).

[5] T. L. Cottrell, "The Strength of Chemical Bonds," Academic Press, Inc., New York, N. Y., 1954, p. 272.

[6] For further elaboration of this point *cf.* C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 322–326.

[7] J. J. Ritter and E. D. Sharpe, THIS JOURNAL, **59**, 2351 (1937).

[8] M. Nakasaki, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **74**, 403, 518 (1953).

[9] M. Nakasaki, *ibid.*, **74**, 405 (1953).

[10] W. E. Lyons, *Nature*, **162**, 1004 (1948).

[11] (a) E. F. P. Harris and W. A. Waters, *ibid.*, **170**, 212 (1952); (b) K. E. J. Barrett and W. A. Waters, *Disc. Faraday Soc.*, **14**, 221 (1953); (c) R. N. Birrell, R. F. Smith, A. E. Trotman-Dickenson, and H. Wilkie, *J. Chem. Soc.*, 2807 (1957).

[12] A. F. Bickel and E. C. Kooyman, *Nature*, **170**, 211 (1952).

[13] S. G. Cohen and C. H. Wang, THIS JOURNAL, **77**, 4435 (1955).

[14] C. Walling and R. Natoli, unpublished work.

thiyl radical on the tertiary hydrogen of cumene. The results of several illustrative runs are presented in Table I.

$$i\text{-Bu-S-S-Bu-}i \xrightarrow{h\nu} 2i\text{-BuS}\cdot \qquad (2)$$

$$i\text{-BuS}\cdot + C_6H_5C(CH_3)_2H \longrightarrow i\text{-BuSH} + C_6H_5C(CH_3)_2\cdot \qquad (3)$$

Immediately obvious from Table I are (1) the initial rate of production of mercaptan is independent of initial disulfide concentration and (2) the extent of conversion of disulfide to mercaptan is independent of both disulfide concentration and light intensity. Figure 1, the mercaptan concentration *vs.* time plot for run 21, represents the typical course followed by all the runs; an initial period when the production of mercaptan is linear with time followed by a rapid leveling of the mercaptan concentration.

TABLE I

THE PHOTOLYSIS OF ISOBUTYL DISULFIDE IN CUMENE (7 *M*)

Run	Variac[a]	Initial RSSR, *M*	Maximum RSH, *M*	Initial rate × 10³, mmole/ml./min.	Conversion, %	f × 10²[b]
19	70	0.209	0.143	0.48	34.3	6.4
20	70	.209	.138	.49	33.1	6.4
21	70	.139	.0965	.48	34.7	4.3
22	70	.0974	.0682	.50	35.1	3.0
23	70	.0695	.0468	.48	33.7	2.2
24	70	.0348	.0241	.50	34.6	1.1
25	55	.146	.099	.425	34.0	4.5
26	90	.146	.100	.605	34.3	4.5

[a] The Variac setting on the lamp power supply determined the light intensity (see Experimental section). [b] f is the fraction of 2537 Å. light initially absorbed by the disulfide, as calculated from Beer's law.

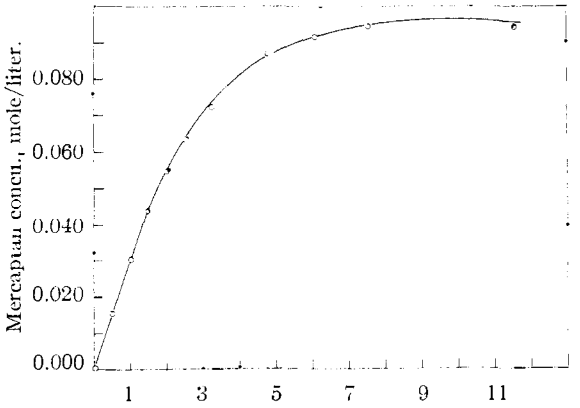

Fig. 1.—A typical mercaptan *vs.* time plot, run 21.

The disulfide concentration varies over a sixfold range in runs 19–24 and the calculated fraction of 2537 Å. light absorbed by the disulfide varies similarly. However, to account for the independence of initial mercaptan production rate of initial disulfide concentration, one must assume that, by some process, the same fraction of the light energy eventually gets to the disulfide in every case. The possibility of isobutyl disulfide forming a complex with cumene having a very high extinction coefficient at 2537 Å. is eliminated by noting that the ultraviolet spectra of mixtures of cumene and isobutyl disulfide (in cyclohexane and 95% ethanol) is that which is calculated from the individual extinction coefficients. The only alternative explanation is that cumene is acting as a photosensitizer. This can occur by two related paths. The first is that the fraction of light initially absorbed by the cumene is re-emitted as fluorescence and immediately absorbed by the disulfide. However, in order to account for the data in Table I, it has to be assumed that this process is 100% efficient; this is not likely.[15] The other possibility is that the fraction of light energy initially absorbed by the cumene is transferred, very rapidly, to the disulfide. Such direct transfer of photochemical excitation energy is well known in the gas phase and has a number of precedents in solution. Thus Bowen and Brocklehurst[16] noted that although 1-chloroanthracene fluoresced *poorly* when irradiated with ultraviolet light, a mixture of 1-chloroanthracene and perylene exhibited a strong fluorescene spectrum of perylene when irradiated with the same intensity of light. Since perylene was transparent at the wave length of light used, this must be an example of direct transfer of photochemical excitation energy. Again, Lunar and Szwarc[17] noted that although diacetyl peroxide does not absorb at all at 3650 Å., it decomposes rapidly in the presence of naphthalene or anthracene on irradiation with light of this wave length.

Runs 28–35 (Tables II and III) were made to study further the possibility that photosensitization by cumene accounts for the independence of initial rate of mercaptan production of the calcu-

TABLE II

MOLAR EXTINCTION COEFFICIENTS OF SUBSTANCES PRESENT IN RUNS 19–35 (2537 Å., IN 95% ETHANOL)

Substance	Molar extinction coefficient
Isobutyl disulfide	366
Isobutyl mercaptan	35
Cumene	162
Benzene	77
Napthalene	2900
Cyclohexane	0

TABLE III

THE PHOTOLYSIS OF ISOBUTYL DISULFIDE IN CUMENE IN THE PRESENCE OF LIGHT SCAVENGERS (35.0°, 70 ON VARIAC, SOLVENT, CYCLOHEXANE)[a]

Run	RSSR, *M*	Cumene, *M*	Initial rate × 10³, mmole/ml./min.	f[b]
28	0.200	0.60	0.33	0.43
29	.200	0.60	.31	.43
30	.200	1.20	.41	.27
31	.200	1.20[c]	.39	.19
32	.200	1.20[d]	.36	.16
34	.200	1.20	.38	.27
35	.200	1.20[e]	.26	.014

[a] Cyclohexane, the solvent, previously had been shown unreactive in this system. [b] f is the fraction of 2537 Å. light initially absorbed by the disulfide, as calculated from Beer's law. [c] 1.52 *M* benzene added. [d] 2.28 *M* benzene added. [e] 1.80 *M* naphthalene added.

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(15) W. West, *Eastman Org. Chem. Bull.*, **28**, #4 (1956).

(16) E. J. Bowen and B. Brocklehurst, *Trans. Faraday Soc.*, **49**, 1131 (1953).

(17) C. Lunar and M. Szwarc, *J. Chem. Phys.*, **23**, 1978 (1953).

lated fraction of 2537 Å. light initially absorbed by the disulfide.

The initial rates of runs 30 and 34, in which the fraction of light initially absorbed by the disulfide is 0.27, are practically the same as those for runs 31 and 32, where the addition of benzene to the system reduces the fraction to 0.19 and 0.16, respectively. More striking is run 35, in which the presence of the strongly absorbing naphthalene reduces the fraction to 0.014, a 20-fold decrease, but the initial rate only from 0.37 to 0.26. Runs 25 and 26 (Table I) show that the initial rate of mercaptan production is quite dependent on light intensity. Therefore, the relative insensitivity of runs 31, 32 and 34 to initial fraction of light absorbed by the disulfide must mean that the other components present (cumene, benzene and naphthalene) are very efficient photosensitizers for this reaction.

The final piece of evidence supporting the photosensitization contention is obtained by the comparison of the absolute intensity of all radiation from the lamp to the initial rate of mercaptan production of run 24 (Table I). The lamp intensity at 35.0° and a Variac setting of 70 is 2.2×10^{20} photons/min. The initial rate of mercaptan production in run 24, 0.50×10^{-3} mmole/ml./min., corresponds to at least 2.25×10^{19} homolytic dissociations of disulfide per minute. Therefore, at least 10% of the total light is involved in dissociation of the disulfide. However, even if one assumes that all the light is 2537 Å., Beer's law calculation (Tables I and II) shows that only 1% of the light is initially absorbed by the disulfide. The rest of the energy reaching the disulfide must be through a photosensitization process. Inherent in the above argument is the assumption that no chain reaction of the type (3) and (4) occurs

$$i\text{-BuS}\cdot + C_6H_5C(CH_3)_2H \longrightarrow i\text{-BuSH} + C_6H_5C(CH_3)_2\cdot \quad (3)$$

$$C_6H_5C(CH_3)_2\cdot + i\text{-BuSS-}i\text{-Bu} \longrightarrow C_6H_5C(CH_3)_2S\text{-}i\text{-Bu} + i\text{-BuS}\cdot \quad (4)$$

Since the chain transfer constant of 2-ethylhexyl disulfide with the radical from styrene (probably less stable than the α,α-dimethylbenzyl radical) at 50° is less than 0.005,[18] corresponding to a rate constant of less than unity in l./mole sec., one would not expect reaction 4 to compete successfully at 35°.

The second significant feature of the photolysis shown in Table I is the leveling off of mercaptan production at approximately 34% conversion independent of both intensity and initial disulfide concentration. Analysis of the reaction mixture at the point of maximum mercaptan concentration reveals considerable unreacted disulfide, eliminating the trivial possibility that the 65% of sulfur unaccounted for has reacted to non-mercaptan products. Two processes may be considered as possibilities for the incomplete conversion of disulfide to mercaptan. The first is the equilibrium

$$i\text{-BuS}\cdot + C_6H_5C(CH_3)_2H \rightleftarrows i\text{-BuSH} + C_6H_5C(CH_3)_2\cdot \quad (5)$$

arising from the reversal of the initial hydrogen abstraction (3). The second is a competing photolysis of mercaptan

$$i\text{-BuSH} \xrightarrow{h\nu} i\text{-BuS}\cdot + H\cdot \quad (6)$$

Equilibrium 5 can be eliminated as the major cause of the leveling off on two counts. If one assumes that the forward reaction proceeds at a constant rate at constant light intensity (the rate of initial mercaptan formation, as we have seen, is independent of disulfide concentration), 5 predicts a constant steady state mercaptan concentration rather than one proportional to initial disulfide as observed. On the other hand, with increasing light intensity and constant disulfide the forward rate of 5 should increase (due to more rapid production of thiyl radicals) leading to an increase in steady state mercaptan concentration, again contrary to observation.

In contrast, if reaction 6 is important, disulfide and mercaptan simply compete for the light energy and mercaptan concentration rises until 6 and the sequence 2–3 occur at approximately the same rate. Obviously this will be determined by the disulfide:mercaptan ratio, independent of disulfide concentration and light intensity. We have also obtained direct evidence of mercaptan photolysis through the detection of molecular hydrogen in the gaseous products of irradiation (run 102). Only traces of H_2S are formed concurrently (run 56) in agreement with the conclusion of Haines, Cook and Ball[19] that mercaptan photolysis involves primarily RS–H cleavage, *i.e.*, the formulation given in reaction 6.

The reactions just discussed imply that, even after mercaptan concentration reaches an approximately steady state, disulfide continues to be converted to further products and the mercaptan is, in effect, recycled. That this is actually the case is shown as follows. With 0.52 *M* disulfide and a Variac setting of 70, steady state mercaptan concentration is reached in under 24 hours. Runs 64–67, irradiated 22 hours, contained 36.7 g. of high boiling residue. In contrast, runs 68–71, irradiated an average of 47 hours, contained 50.1 g., an increase of almost 50%. The composition of such residues is considered in the next section.

Product Analysis of the Irradiation of Isobutyl Disulfide in Cumene.—Our original conception of the mechanism of the photolysis of isobutyl disulfide in cumene at 35° led to this scheme as the reaction mechanism

$$i\text{-Bu-S-S-}i\text{-BuS} \xrightarrow{h\nu} 2\ i\text{-BuS}\cdot \quad (2)$$

$$i\text{-BuS}\cdot + C_6H_5C(CH_3)_2H \longrightarrow i\text{-BuSH} + C_6H_5C(CH_3)_2\cdot \quad (3)$$

$$2C_6H_5C(CH_3)_2\cdot \longrightarrow C_6H_5C(CH_3)_2C(CH_3)_2C_6H_5 \text{ (dicumene)} \quad (7)$$

$$C_6H_5C(CH_3)_2\cdot + i\text{-BuS}\cdot \longrightarrow C_6H_5C(CH_3)_2S\text{-}i\text{-Bu} \quad (8)$$

If termination occurs exclusively by reaction 7, then two moles of mercaptan will be produced per mole of disulfide consumed. If 8 occurs exclusively, then a 1:1 stoichiometry will exist.

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[18] R. M. Pierson, A. J. Costanza and A. J. Weinstein, *J. Polymer Sci.*, **17**, 221 (1955).

[19] W. E. Haines, G. L. Cook and J. S. Ball, THIS JOURNAL, **78**, 5213 (1956).

A concurrent disulfide and mercaptan analysis was carried out for run 54 (5.32 g. of isobutyl disulfide diluted to 150 ml. with cumene). The analysis results are presented in Table IV.

TABLE IV

CONCURRENT DISULFIDE AND MERCAPTAN ANALYSIS DURING THE PHOTOLYSIS OF A MIXTURE OF ISOBUTYL DISULFIDE IN CUMENE (35°, 70 ON VARIAC)

Time, min.	[RSH], *M*	[RSSR], *M*	$\frac{[\mathrm{RSH}]}{[\mathrm{RSSR}]_0 - [\mathrm{RSSR}]}$
0	0.000	0.202	..
55	.039	.175	1.44
100	.061	.157	1.36
150	.088	.140	1.42
220	.112	.124	1.43
320	.134	.099	1.30
1260	.140	.048	0.91

Although the data indicate that both 7 and 8 are occurring, work-up of run 17 (8.37 g. of isobutyl disulfide diluted to 150 ml. with cumene and irradiated for 22 hours, final mercaptan concentration 0.211 *M*) reveals no α,α-dimethylbenzyl isobutyl sulfide and only 40% of the dicumene calculated assuming reaction 7 occurs exclusively.

The above data, coupled with the fact that only a negligible amount of H_2S is produced during the photolysis, makes it clear that sulfur is being incorporated into some unidentified product or products. A very large scale work-up was made by combining the irradiation mixtures of nine runs. The isobutyl mercaptan, excess cumene and unreacted isobutyl disulfide were removed by distillation and the resultant residue subjected to chromatography, distillation, molecular distillation, oxidation, etc. (see Experimental section for details). Only 24% of the residue is identified as dicumene. The rest of the residue is a complex mixture of sulfides, some possessing molecular weights of over 400 and containing at least three atoms of sulfur per molecule. The majority of this material is essentially immobile at room temperature. α,α-Dimethylbenzyl isobutyl sulfide (I) and isobutyl 2-methyl-2-phenylethyl sulfide (II) are isolated in very small quantities from the above mixture and unambiguously identified by

$$C_6H_5C(CH_3)_2S\text{-}Bu\text{-}i \ \ (\text{I}) \qquad C_6H_5CH(CH_3)CH_2S\text{-}Bu\text{-}i \ \ (\text{II})$$

oxidation to their sulfones. Sulfide I arises simply from the dimerization of an α,α-dimethylbenzyl (cumyl) radical with an isobutyl thiyl radical. It was puzzling why only a very small amount of I formed relative to the other simple dimer, dicumene. However, when a dilute solution of I in cumene is irradiated under the usual conditions, work-up of the reaction mixtures reveals that none of it remains. Instead, some dicumene forms as well as a series of sulfides very similar in chromatographic properties to those obtained in the large scale work-up of the isobutyl disulfide–cumene system. Apparently I is subject to photochemical decomposition, the resulting radicals undergoing reactions 3, 7 and the further processes discussed below.

$$C_6H_5C(CH_3)_2S\text{-}Bu\text{-}i \xrightarrow{h\nu} C_6H_5C(CH_3)_2\cdot + i\text{-}BuS\cdot \quad (9)$$

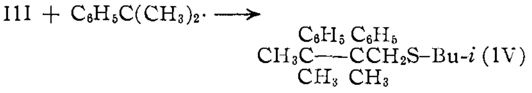
The other sulfide, II, corresponds to the free radical adduct of isobutyl mercaptan and isopropenylbenzene. Isopropenylbenzene can arise by a disproportionation reaction between a cumyl radical and, for example, an isobutyl thiyl radical. Similar types of disproportionations have been observed previously. The disproportionation of a *p*-cymyl radical (*p*-tolyl-$C(CH_3)_2\cdot$) to *p*-isopropenyltoluene is proposed to account for some of the products found in the oxidative coupling of *p*-cymene.[20] Furthermore, the room temperature photochemical dehydrogenation of tetralin, cyclohexene and squalene by benzothiazyl disulfide[8] apparently involves successive hydrogen abstractions and disproportionations. Thus, the isolation of II certainly implies strongly that isopropenylbenzene exists as a transient species in the reaction. The ability of the system to scavenge isopropenylbenzene is demonstrated by deliberately adding small increments of it to an irradiation mixture at various points in the reaction. Mercaptan production completely halts, starting again apparently when all the isopropenylbenzene is consumed (Fig. 2).

The existence of isopropenylbenzene as an intermediate in the photolysis of isobutyl disulfide in cumene readily accounts for the complex, high molecular weight mixture containing several sulfur atoms per molecule obtained as the major portion of the reaction products, *via* steps such as

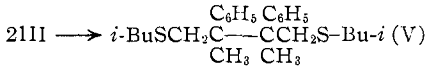
$$C_6H_5C(CH_3)_2\cdot + i\text{-}BuS\cdot \longrightarrow C_6H_5C(CH_3){=}CH_2 + i\text{-}BuSH \quad (10)$$

$$C_6H_5C(CH_3){=}CH_2 + i\text{-}BuS\cdot \longrightarrow C_6H_5\text{–}\dot{C}(CH_3)CH_2S\text{–}Bu\text{-}i \ \ (\text{III}) \quad (11)$$

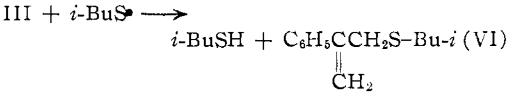
$$\text{III} + i\text{-}BuSH \longrightarrow i\text{-}BuS\cdot + C_6H_5CH(CH_3)CH_2S\text{–}Bu\text{-}i \ (\text{II}) \quad (12)$$



$$\text{III} + C_6H_5C(CH_3)_2\cdot \longrightarrow CH_3\overset{C_6H_5}{\underset{CH_3}{C}}\text{——}\overset{C_6H_5}{\underset{CH_3}{C}}CH_2S\text{–}Bu\text{-}i \ (\text{IV}) \quad (13)$$



$$2\text{III} \longrightarrow i\text{-}BuSCH_2\overset{C_6H_5}{\underset{CH_3}{C}}\text{——}\overset{C_6H_5}{\underset{CH_3}{C}}CH_2S\text{–}Bu\text{-}i \ (\text{V}) \quad (14)$$



$$\text{III} + i\text{-}BuS\bullet \longrightarrow i\text{-}BuSH + C_6H_5\underset{\underset{CH_2}{\|}}{C}CH_2S\text{–}Bu\text{-}i \ (\text{VI}) \quad (15)$$

Steps 10–14 are self-explanatory. Step 15 involves another disproportionation to give VI, which, in turn, may add any radical in the system. The resultant radical can then dimerize with any radical available or disproportionate. It is clear how a very complex mixture can result from a series of successive additions and disproportionations.

Since more than 75% of the reaction mixture residue is this complex sulfide mixture, it is probable that the fate of the majority of the cumyl radicals is disproportionation. Assuming 11 occurs readily, then IV and V should be a major portion of the residue. The search for them was concentrated in the chromatographic fraction eluted by hexane because they are relatively simple sulfides. A portion of this fraction, when oxidized to the sulfone and rechromatographed, reveals two main components. They are solid, but not crystalline, and probably somewhat impure. Quantitative ele-

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(20) H. Pines, B. Kvetinskas and V. N. Ipatieff, THIS JOURNAL, **77**, 343 (1955).

mental analyses as well as molecular weight determinations are in fair agreement with the sulfones of IV and V.

Other Systems. *t*-Butyl Disulfide–Cumene.—The photolysis of *t*-butyl disulfide in cumene (run 2R, 8.5 g. of *t*-butyl disulfide diluted to 150 ml. with cumene, 25°, 70 on variac) follows a course very similar to isobutyl disulfide in cumene; an initial linear mercaptan production with time followed by a fairly rapid leveling off of the mercaptan concentration. However, the total conversion observed in this system is only 2%. Analysis of the reaction mixture indicates that most of the disulfide is unreacted. Removal of the *t*-butyl mercaptan by distillation and re-irradiation results in the formation of more mercaptan. The mercaptan concentration again levels at the same point. When a mixture of *t*-butyl disulfide and cumene containing more than the steady-state concentration of mercaptan is irradiated, the mercaptan concentration drops very rapidly to the steady-state point. The above observations indicate that the leveling off of this system probably is due to the same reason as in the isobutyl disulfide–cumene system; a point is reached at which the rate of mercaptan production from the attack of thiyl radical on cumene becomes equal to the rate at which the mercaptan is photochemically destroyed.

Isobutyl Disulfide and Other Compounds.—The photolysis of isobutyl disulfide in a series of compounds all possessing more or less labile hydrogens was investigated. All runs were made by diluting 5.32 g. of isobutyl disulfide to 150 ml. with solvent and then irradiating until the mercaptan concentration remained constant. Table V lists the results of this study.

TABLE V

THE PHOTOLYSIS OF ISOBUTYL DISULFIDE IN A SERIES OF SUBSTRATES, 35.0°

Run[a]	Compound	Conversion, %	Initial rate × 10^3, mmole/ml./min.
19–20	Cumene	34	0.49
36	Isopropyl ether	7.8	.23
37	Diethyl malonate	1.5	.07
38	Fluorene[b]	6.0	.22
39	Benzaldehyde	2.5	.23
40	*sec*-Butyl alcohol	6.5	.08
41	Anisaldehyde	0.5	Very small
42	*p*-Cymene	41	0.49
43–45	Cumene	35	.64
46	Diphenylmethane	25	.25
47	Tetralin	39	.36
48	Benzyl ether	10	Erratic
49	α-Methyl benzyl ether	4.5	Erratic

[a] Runs 19–42 were made with lamp 1, while 42–49 were made with lamp 2. [b] 0.45 *M* in cyclohexane.

Since the data of Table V represent merely a quick survey to illustrate the scope of hydrogen abstraction reactions by thiyl radicals under our experimental conditions, we shall make no attempt to discuss them in detail.

Experimental

Materials.—The cumene and isobutyl disulfide used were middle fractions from the distillation of Eastman Kodak Co. white label grade material. Cyclohexane, Eastman Kodak Co. white label grade, and thiophene-free benzene, Mallinckrodt analytical grade, were used without further purification. Matheson isopropenylbenzene was distilled and only the middle fraction used. Woelm alumina, activity grade 1, non-alkaline (almost neutral), was used for all chromatographic separations.

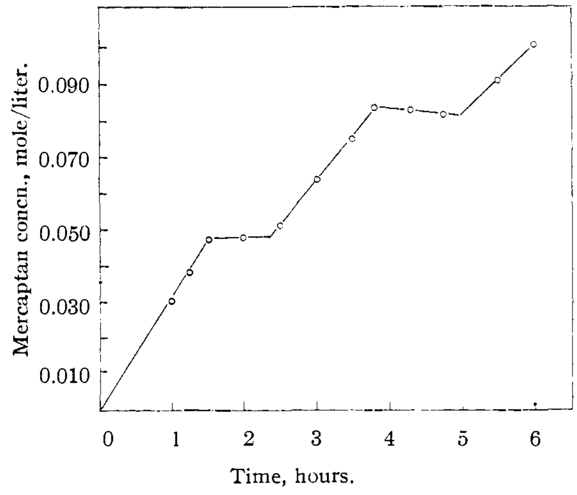

Fig. 2.—The scavenger effect of isopropenylbenzene.

α,α-Dimethylbenzyl Isobutyl Sulfide.—To a solution of 14.5 g. of isobutyl mercaptan (0.16 mole) and 21.6 g. of isopropenylbenzene (0.18 mole) in 100 ml. of glacial acetic acid was added 10 drops of 18 *M* sulfuric acid. After standing in the dark at room temperature for 2 hours, the characteristic mercaptan odor was gone. The mixture was diluted with 75 ml. of water and extracted with four 30-ml. portions of CCl_4. Evaporation of the CCl_4 left a clear liquid (yellow) residue which was distilled through a 5-inch vacuum-jacketed Vigreux column; 28 g. (90%), b.p. 74–78° (0.3 mm.), $n^{25}D$ 1.5215. This clear, colorless distillate was redistilled through a 12-inch silvered, vacuum-jacketed Vigreux column, b.p. 66.0–67.7° (0.1 mm.), $n^{25}D$ 1.5221.

Anal. Calcd. for $C_{13}H_{20}S$: C, 75.00; H, 9.63; S, 15.37. Found: C, 75.11; H, 9.48; S, 15.20, 15.35.

α,α-Dimethylbenzyl Isobutyl Sulfone.—α,α-Dimethylbenzyl isobutyl sulfide (2.89 g., 0.014 mole) was cooled to −80° and 10 ml. of Becco 40% peracetic acid was added slowly over a period of 2 minutes. A vigorous reaction took place and the reaction mixture was allowed to warm to room temperature. The addition of water resulted in the formation of a white precipitate, 2.74 g. (82%), m.p. 112–113°, after 2 recrystallizations from 25% ethanol. The infrared spectrum showed the typical strong sulfone peaks at 7.7 and 8.8 μ.

Isobutyl 2-Methyl-2-phenylethyl Sulfide.—A solution of 20.7 g. of isobutyl mercaptan (0.23 mole), 27.1 g. of isopropenylbenzene (0.18 mole) and 0.40 g. of benzoyl peroxide (0.0017 mole) in 90 ml. of hexane was refluxed for 6 hours. The solvent, excess mercaptan and unreacted isopropenylbenzene were removed by distillation leaving a clear yellow liquid residue, which was distilled through a 5-inch vacuum-jacketed Vigreux column, b.p. 86–93° (0.3 mm.), $n^{25}D$ 1.5192. This material was redistilled through a 12-inch silvered, vacuum-jacketed Vigreux column, b.p. 71–73° (0.1 mm.), $n^{25}D$ 1.5189. Gas chromatographic analysis of this distillate showed it to be free of the isomeric α,α-dimethylbenzyl isobutyl sulfide.

Anal. Calcd. for $C_{13}H_{20}S$: C, 75.00; H, 9.63; S, 15.37. Found: C, 74.80; H, 9.41; S, 15.41, 15.23.

Isobutyl 2-Methyl-2-phenylethyl Sulfone.—Isobutyl 2-methyl-2-phenylethyl sulfide (7.33 g., 0.035 mole) was treated with 20 ml. of peracetic acid in a manner analogous to the preparation of α,α-dimethylbenzyl isobutyl sulfone. Upon the addition of water, oil globules formed and rapidly fell to the bottom of the flask. The mixture was extracted four times with 30-ml. portions of CCl_4, the CCl_4 removed by distillation, leaving 7.63 g. (90%) of viscous liquid. Another 7.01 g. of sulfide was oxidized and 7.17 g. (88%) of the sulfone was obtained. These liquids were combined and distilled through a 5-inch vacuum-jacketed Vigreux column, b.p. 140–142° (0.1 mm.), $n^{25}D$ 1.5160.

Anal. Calcd. for $C_{13}H_{20}O_2S$: C, 65.00; H, 8.34; S, 13.33. Found: C, 65.44, 65.30; H, 8.16, 7.99; S, 13.29, 13.26.

2,3-Dimethyl-2,3-diphenylbutane (Dicumene).—Dicumene was prepared by a method similar to that of Kharasch, McBay and Urry.[21] A mixture of 51.4 g. of Lucidol di-*t*-butyl peroxide (0.35 mole) and 214 g. of cumene was refluxed overnight. The acetone, *t*-butyl alcohol, unreacted peroxide and cumene were removed by vacuum distillation leaving 30.5 g. of a white crystalline residue, m.p. 117–118° after 2 recrystallizations from 95% ethanol; reported 115°,[21] 115–116°[20] and 113–114°.[22]

The Irradiation System.—The ultraviolet irradiation apparatus used in this work consisted of a lamp, irradiation vessel and sampler which was very similar to that described by Kharasch.[23] The lamp was a quartz coil (8-mm. outside diameter) cold electrode-type filled with approximately 4 mm. of argon and a few drops of very pure mercury. It was operated by means of a General Electric 51G high voltage transformer fed through a Variac variable transformer by which the light intensity was controlled. According to Noyes and Leighton[24] under these conditions 90% or more of the radiation emitted between 1800 and 10000 Å. is confined to the mercury resonance lines at 1849 and 2537 Å. The irradiation vessel into which the lamp was fitted had a volume of approximately 180 ml. (with the lamp in it). At the bottom was a sintered glass disk through which nitrogen was bubbled slowly during all irradiations as well as for 0.5 hour before turning the lamp on. The vessel was surrounded by a water jacket through which water at constant temperature was circulated at high speed by means of a circulating thermostat. Samples for analysis were withdrawn from the reaction mixture by means of an outlet near the bottom of the vessel with the aid of the sampler delivering approximately 2 cc. A uranyl oxalate actinometer consisting of 0.002 *M* uranyl oxalate and 0.01 *M* oxalic acid was used for the calibration of the lamp. Such a system was shown adequate by Forbes and Heidt.[25] Uranyl oxalate was prepared by mixing hot solutions of 50 g. of uranyl acetate (0.12 mole) in 750 ml. of water and 35 g. of oxalic acid dihydrate (0.39 mole) in 250 ml. of water. The yellow precipitate which formed when the solutions cooled was dried at 110° for three hours. Titration with potassium permanganate was in excellent agreement with the formula $UO_2C_2O_4$. Using 0.5 as the quantum yield for the actinometer,[26] the over-all light intensities at Variac settings 55, 70 and 90 (35.0°) were found to be 1.75, 2.22 and 2.74 $\times 10^{20}$ photons/minute, respectively.

Mercaptan and Disulfide Analysis.—Mercaptan was determined by an amperometric titration with $AgNO_3$.[27] A Sargent synchronous motor, type KYC-22, was used to rotate the platinum electrode. Disulfide was determined by passage through a Jones reductor at 60° followed by amperometric titration of the resulting mercaptan.[28]

Hydrogen Sulfide in the Gaseous Products of the Photolysis.—A solution of 13.156 g. of isobutyl disulfide (run 56) in 135 ml. of cumene was placed into the irradiation vessel. The outlet of the reaction vessel was connected successively to calcium chloride and lead acetate trihydrate tubes. Under these conditions only H_2S is absorbed in the lead acetate tube.[29] The lamp was turned on while nitrogen was bubbled slowly through the solution. After 22 hours the mercaptan concentration was 0.349 *M;* however, only 71 mg. of lead sulfide was found in the lead acetate tube.

Hydrogen in the Gaseous Products of the Photolysis.—A solution of 14.810 g. of isobutyl disulfide (run 102) in 165 ml. of cumene was placed into the irradiation vessel. The following were connected successively to the outlet of the lamp; a 10-inch water-jacketed condenser, a lead acetate tube, a gas sample tube, a paraffin oil trap and finally a gas buret. Nitrogen was bubbled through the system at the rate of 50 ml. per minute for 35 minutes and then turned off. The irradiation now was started and after 68.5 hours 253 ml. of gas had formed. The gas was analyzed on a mass spectrometer. In order to prevent any hydrocarbon material from entering the instrument, the gas sample tube was cooled in liquid nitrogen; no condensation was observed. The analysis revealed that the gas was quite rich in hydrogen. The ratio of H^2 to N^{28} peaks was 0.84 whereas the corresponding ratio in Matheson prepurified nitrogen was 9.3×10^{-4}.

The Photolysis of α,α-Dimethylbenzyl Isobutyl Sulfide in Cumene.—α,α-Dimethylbenzyl isobutyl sulfide (4.015 g.) (run 200C) in 135 ml. of cumene was irradiated for 26 hours at 35.0°, Variac setting 70. Nitrogen was bubbled through the system continuously and the gaseous stream passed through a trap at −80°. The contents of the trap revealed approximately 0.1 ml. of liquid which has a very distinct mercaptan odor. Gas chromatographic analysis, however, showed that it was almost all cumene. The excess cumene was removed from the yellow reaction mixture by distillation (10 mm.) leaving 3.95 g. of a fairly mobile yellow liquid residue. The portion of this soluble in hexane, 3.65 g., was applied to a 100-g. alumina column and 50-ml. fractions taken. Table VI summarizes the results of the chromatography.

TABLE VI

CHROMATOGRAPHIC SEPARATION OF THE PRODUCTS FROM PHOTOLYSIS OF α,α-DIMETHYLBENZYL ISOBUTYL SULFIDE IN CUMENE

Fractions	Solvent	Appearance	Weight, g.
2–3	Hexane	White solid	0.642
4–6	Hexane	Sl. yell. mobile oil	0.335
7–9	Benzene	Deep	1.66
10–12	Ether	yellow	0.490
13–14	Methanol	immobile oil	0.246

Chromatography of pure α,α-dimethylbenzyl isobutyl sulfide revealed that it was eluted rather readily from alumina with hexane. Since peracetic acid oxidation of fractions 4–6 gave no solid product, it was concluded that all the α,α-dimethylbenzyl isobutyl sulfide had been photolyzed. After 4 recrystallizations from 95% ethanol, the solid present in fractions 2 and 3 melted from 116.5–118.0°. A mixed melting point with an authentic sample of dicumene showed no depression.

Chromatographic Separation of Synthetic α,α-Dimethylbenzyl Isobutyl Sulfone (VII) and Isobutyl 2-Methyl-2-phenylethyl Sulfone (VIII).—Sulfone VII (0.350 g.) and 0.670 g. of VIII were dissolved in hexane and applied to a 100-g. alumina column. No material came off the column with hexane, 1:1 hexane–benzene and benzene. Elution with 5% ether in benzene gave a white solid. Elution was continued with this solvent until no more material came off the column. The solid was identified as VII by its infrared spectrum (0.112 g., 32%). Chromatography was continued with 30% ether in benzene and a viscous liquid came off the column, identified by its infrared spectrum as VIII (0.248 g., 37%). This experiment showed that the separation of the sulfides of VII and VIII (which both come off a chromatographic column with the same solvent, hexane) may be accomplished by conversion to the corresponding sulfones and subsequent chromatography.

Large Scale Work-up of the Reaction Mixture from the Photolysis of Isobutyl Disulfide in Cumene.—Runs 83–91 were made by irradiating mixtures of 14 g. of isobutyl disulfide (0.079 mole) and 135 ml. of cumene for an average of about 50 hours. The resultant reaction mixtures were combined and the isobutyl mercaptan, excess cumene and unreacted isobutyl disulfide were removed by distillation. A solid precipitated in the 158.5 g. of orange-red residue upon standing overnight. This mixture was triturated with hexane and 13.4 g. of a tan solid was recovered. Recrystallization once from 95% ethanol resulted in a white crystalline solid, m.p. 116–118°. The filtrate from the above trituration was applied to an 1800-g. alumina column. The mixture then was chromatographed using hexane, ben-

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(21) M. S. Kharasch, H. C. McBay and W. H. Urry, *J. Org. Chem.*, **10**, 401 (1945).

(22) H. C. McBay and P. T. Groves, *ibid.*, **21**, 691 (1956).

(23) M. S. Kharasch and H. N. Friedlander, *ibid.*, **14**, 239 (1949).

(24) W. A. Noyes and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publishing Corp., New York, N. Y., 1941, p. 38.

(25) G. S. Forbes and L. J. Heidt, THIS JOURNAL, **56**, 2363 (1934).

(26) W. G. Leighton and G. S. Forbes, *ibid.*, **52**, 3139 (1930).

(27) I. M. Kolthoff and W. E. Harris, *Ind. Eng. Chem., Anal. Ed.*, **18**, 161 (1946).

(28) I. M. Kolthoff, D. R. May, P. Morgan, H. A. Laitinen and A. S. O'Brien, *ibid.*, **18**, 442 (1946).

(29) W. Segal and R. L. Starkey, *Anal. Chem.*, **25**, 1645 (1953).

zene, ether and finally methanol as solvents. Each fraction was approximately 200 ml. Table VII summarizes the results of the chromatography.

TABLE VII

CHROMATOGRAPHIC SEPARATION OF THE PRODUCTS FROM THE IRRADIATION OF ISOBUTYL DISULFIDE IN CUMENE

Fractions	Solvent	Residue appearance	Weight, grams	Quantitative analysis C	H	S	Mol. wt.
1–5	Hexane	Solid + red oil	101.5	...	..	...	..
6–22	Hexane	Deep or. mob. oil	5.1	76.44	9.35	14.30	290
24–33	Benzene	Very viscous	18.5	73.89	8.97	17.66	357
34–42	Ether	oil	6.5	72.06	8.91	18.53	395
43–45	Methanol	Very sl. mob. brown oil	9.9	72.08	8.84	17.08	327

The total amount recovered, 142.7 g. (98%)

Upon standing overnight, crystals formed in the 101.5 g. residue of fractions 1–5. The mixture was filtered and the solid washed with 30% acetone in methanol. One recrystallization of the 15.0 g. of solid gave a white crystalline material, m.p. 115–118°.

The 80 g. of filtrate from above was distilled through a 5-inch vacuum-jacketed Vigreux column. The first fraction, 17 g., b.p. 47° (0.5 mm.), was identified as isobutyl disulfide. Fraction 3, 4.9 g., b.p. 80–99° (0.5 mm.), $n^{26}\mathrm{D}$ 1.5217, was a clear yellow liquid. Fraction 4, b.p. 99–125° (0.5 mm.), was a mixture of a yellow liquid and a solid. Filtration gave 10.3 g. of liquid, $n^{25}\mathrm{D}$ 1.5331, as well as 5.20 g. of solid. This solid was recrystallized once from 95% ethanol, m.p. 116–118°. The 45.5-g. pot residue of the distillation was a wine-colored viscous liquid.

The three crystalline products obtained above had the same melting point and apparently were identical. A carefully ground mixture of equal portions of each of them melted between 115.5 and 118.0°. This mixture was recrystallized once from 95% ethanol, m.p. 117–118°. It did not depress the melting point of authentic dicumene.

Anal. Calcd. for $C_{18}H_{22}$: C, 90.75; H, 9.25; mol. wt., 238. Found: C, 90.62; H, 9.38; mol. wt., 223.

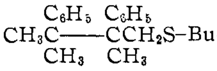
Fraction 3 of the above distillation was combined with a similar fraction (5.0 g.) obtained from the work-up of 9 other runs (68–71, 76–80) and the resultant mixture distilled. Fraction 2 (1.5 g., b. p. 60–66° (0.05 mm.) reacted violently with 5 ml. of peracetic acid. Addition of water to the oxidation mixture resulted in a white precipitate, m.p. 112–113° after one recrystallization from 50% ethanol. This corresponds exactly to the melting point of the synthetic α,α-dimethylbenzyl isobutyl sulfone. Their infrared spectra in KBr were identical in every respect. A mixed melting point showed a small depression (m.p. 107–110°).

Anal. Calcd. for $C_{13}H_{20}O_2S$: C, 65.00; H, 8.34; S, 13.33. Found: C, 65.08, 65.00; H, 8.34, 8.41; S, 13.38, 13.42.

Fractions 3 and 4 (combined 4.0 g.), b.p. 66–74° (0.05 mm.), were oxidized with 10 ml. of peracetic acid. Upon the addition of water to the oxidation mixture, globules formed which rapidly fell to the bottom of the flask. This mixture was extracted with CCl_4, the CCl_4 removed, leaving 3.0 g. of a viscous liquid. This liquid was chromatographed on a 300-g. alumina column; 1.0 g. of a viscous liquid was eluted with 30% ether in benzene. The infrared spectrum of this oil was identical in every respect with that of synthetic isobutyl 2-methyl-2-phenylethyl sulfone and quite different from α,α-dimethylbenzyl isobutyl sulfone. The 1.0 g. of oil was subjected to molecular distillation (85°, 0.3 mm.) and it distilled almost completely. The nuclear magnetic resonance spectrum of the distillate was identical with that of synthetic isobutyl 2-methyl-2-phenylethyl sulfone. Furthermore, their indices of refraction were very similar; distillate, $n^{25}\mathrm{D}$ 1.5155; synthetic material, $n^{25}\mathrm{D}$ 1.5161.

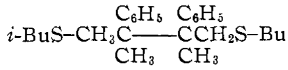
Anal. Calcd. for $C_{13}H_{20}O_2S$: C, 65.00; H, 8.34; S, 13.33. Found: C, 65.07, 64.82; H, 8.53, 8.59; S, 14.12, 14.16.

Work-up of the residue of the distillation of fractions 1–5 of the main chromatography: The search for IV and V was directed toward the 45.5-g. residue of the distillation of fractions 1–5 of the main chromatography. The residue was subjected to molecular distillation at 0.001–0.005 mm. Table VIII summarizes the results of the distillation.



$$CH_3\overset{C_6H_5}{\underset{CH_3}{C}}\text{——}\overset{C_6H_5}{\underset{CH_3}{C}}CH_2S\text{–}Bu\text{-}i$$

IV



$$i\text{-}BuS\text{–}CH_2\overset{C_6H_5}{\underset{CH_3}{C}}\text{——}\overset{C_6H_5}{\underset{CH_3}{C}}CH_2S\text{–}Bu\text{-}i$$

V

TABLE VIII

MOLECULAR DISTILLATION OF THE RESIDUE OF THE DISTILLATION OF FRACTIONS 1–5 OF THE MAIN CHROMATOGRAPHY

Fraction	Bath temp., °C.	System temp., °C.	Orange oil G.	$n^{25}\mathrm{D}$
1	To 160	To 145	4.61	1.5455
2	To 195	To 175	14.76	1.5495
3	To 225	To 200	5.21	1.5529

Fraction 2 (6.0 g.) was oxidized with 25 ml. of peracetic acid at 0°. After standing for one hour at room temperature, the addition of water resulted in the formation of an oil. This was extracted with CCl_4, the extract dried over magnesium sulfate and the CCl_4 removed. A 5.3-g. yield of an orange glass resulted. The infrared spectrum showed strong absorption at 7.7 and 8.8 μ, characteristic of sulfones. This residue was dissolved in a 1:1 hexane–benzene solution and applied to a 500-g. alumina column; 0.375 g. of a quite mobile liquid was eluted with the first solvent, 1:1 hexane–benzene. Pure benzene and 5% benzene in ether brought nothing more off the column; 0.860 g. of an orange glass (A) was obtained using 30% ether in benzene. Nothing further was obtained, even with pure ether; 1.82 g. of an orange glass (B) was eluted using 2% methanol in ether. Fraction A was rechromatographed on 100 g. of alumina and the 30% ether in benzene fractions combined; B was rechromatographed on 200 g. of alumina and the 2% methanol in ether fractions combined. The rechromatographed A and B were dissolved in ether and filtered through sintered glass funnels into 10-ml. erlenmeyer flasks. These were evacuated at 0.2 mm. (100°) for four hours.

On this basis of the polarity of the solvents necessary to elute A and B, if A and B are the sulfones of IV and V, then A should be the sulfone of IV and B should be the sulfone of V.

Anal. of (A): calcd. for sulfone of IV, $C_{22}H_{30}O_2S$: C, 73.60; H, 8.45; S, 8.98; mol. wt., 358. Found: C, 73.65; H, 10.48; S, 9.50; mol. wt., 409. (B): Calcd. for sulfone of V, $C_{26}H_{38}O_4S_2$: C, 65.30; H, 7.94; S, 13.40; mol. wt., 478. Found: C, 65.12; H, 8.37; S, 11.86; mol. wt., 458.

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