Biologically Oriented Organic Sulfur Chemistry.
V. Alkanesulfenyl Iodides[1]

Lamar Field,[1d] Janice L. Vanhorne,[1d] and Leon W. Cunningham[1e]

*Departments of Chemistry and Biochemistry, Vanderbilt University,
Nashville, Tennessee 37203*

To provide a better basis for understanding biochemically important sulfenyl iodides (RSI), syntheses and properties of 2-methyl-2-propanesulfenyl iodide (3) were studied. Five syntheses gave 3 in yields of 51-92% with uv ϵ_{max} values in reasonable agreement, *viz.*: addition of silver 2-methyl-2-propanethiolate (2) to I_2, and of I_2 to 2; treatment of a sulfenamide with hydriodic acid; and treatment of 2-methyl-2-propanethiol with iodine chloride or with I_2. Average values for 3 were ϵ_{444} 64 and ϵ_{280} 356 in methylcyclohexane (determined by estimating excess I_2 titrimetrically or spectrophotometrically) and ϵ_{444} 75 in carbon tetrachloride (determined through nmr measurement of 3); charge transfer complexes did not seem to be involved, *e.g.*, of 3 with I_2 or iodide ion. The values of ϵ_{max} in methylcyclohexane were approximately confirmed by photolysis of 3 to *t*-butyl disulfide and I_2, during which 3 disappeared as I_2 formed. This reaction was zero order; it confirmed the structure of 3. The structure of 3 was further confirmed by nmr (δ 1.45) and by converting it to a known unsymmetrical disulfide and sulfenamide (during which time the spectrum of 3 disappeared as that of the sulfenamide appeared). Nearly all of 3 survived at $-12°$ in the dark for more than 11 days, but at ambient conditions only about half survived for 3 days. Survival of 3 was enhanced by dilution, was little effected by water or iodide ions, and was decreased by thiosulfate or triiodide ions. Apparently, silver 1-butane- or 2-butanethiolate with I_2 gave no sulfenyl iodide, but triphenylmethanethiol with I_2 did.
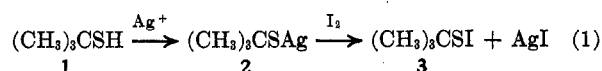
Sulfenyl iodides (RSI), often postulated as intermediates without having been characterized,[2] seem to be biochemically important. Tobacco mosaic virus forms a stable sulfenyl iodide,[3] and other proteins later were found to do so as well;[4,5] sulfenyl iodides may mediate protein iodination.[6]

Since β-lactoglobulin sulfenyl iodide reacts much more rapidly with antithyroid agents such as thiouracil than with more typical thiols such as 2-hydroxyethanethiol, Cunningham suggested that antithyroid activity might depend upon the reaction between the sulfenyl iodide and the antithyroid agent and therefore that a protein sulfenyl iodide may be a reactive key intermediate in thyroidal iodine metabolism.[7] Others also have speculated on this possibility,[6,8] and evidence now is beginning to appear that iodination of tyrosine moieties in the thyroid gland may indeed involve sulfenyl iodides.[9,10]

The possibility that thyroidal iodination involves a protein sulfenyl iodide points to the desirability of more information regarding simple well defined sulfenyl iodides. This paper contributes such information.

Rheinboldt and Motzkus reported 31 years ago on a simple model, 2-methyl-2-propanesulfenyl iodide (3).

They prepared 3 by converting the thiol 1 to the silver thiolate (2), or (usually) to the mercuric thiolate, and adding the thiolate to I_2 in dry ether at 0-20° (eq 1).[11]

$$(CH_3)_3CSH \xrightarrow{Ag^+} (CH_3)_3CSAg \xrightarrow{I_2} (CH_3)_3CSI + AgI \quad (1)$$
$$1 \qquad\qquad\qquad 2 \qquad\qquad\qquad 3$$

The reactivity of 3 precluded its isolation in a pure state. Oxidation of 1 with I_2 also has been reported to give 3, but only incidentally and with only the substantiation that the solution turned yellow, then brown, and that the "unforgettable and unmistakable smell of sulfenyl iodides developed."[12] An as yet unpublished preparation of triphenylmethanesulfenyl iodide by Ciuffarin and Tentori also has been mentioned.[13]

Preparation of 3.—Since 3 is best handled in solution, knowledge of its uv extinction coefficients would be helpful in following it. Determination of ϵ_{max} is complicated by such features as the absorption of *t*-butyl disulfide (4) and the possibility of extraneous species such as charge transfer complexes. In obtaining values of ϵ_{max} therefore, we ensured reliability by using a variety of syntheses, *viz.*, two variations of the Rheinboldt-Motzkus procedure (procedures A and B, each with four subsidiary analytical determinations), as well as three other syntheses (procedures C-E). The results are summarized in Table I. (Beforehand, as related later, the identity of 3 was confirmed and the spectra were studied extensively.)

Procedure A was like that of Rheinboldt and Motzkus, except that an inert solvent was used to minimize charge transfer complexes. The thiolate 2 was added to I_2, and the unconsumed I_2 then was determined in two ways: titrimetrically, by adding thiosulfate and back-titrating the excess with I_2, and spectrophotometrically, from the absorbance of I_2 before the thiosulfate wash (both our experience and that of Rheinboldt and Motzkus show 3 to be stable to thiosulfate under these conditions).

(1) (a) Paper IV: L. Field and C. H. Foster, *J. Org. Chem.*, **35**, 749 (1970). (b) This investigation was supported by Public Health Service Research Grant No. AM11685 from the National Institute of Arthritis and Metabolic Diseases. (c) Taken from part of the M.S. thesis of J. L. V., Vanderbilt University, Jan 1970; the thesis may be consulted for greater detail. (d) Department of Chemistry, Vanderbilt University, Nashville, Tenn. (e) Department of Biochemistry, Vanderbilt University, Nashville, Tenn.

(2) (a) N. Kharasch, "Organic Sulfur Compounds," Vol. I, Pergamon Press, New York, N. Y., 1961, p 387. (b) I. M. Kolthoff and W. E. Harris, *Anal. Chem.*, **21**, 963 (1949). (c) J. P. Danehy, *Quart. Rep. Sulfur Chem.*, **2**, 325 (1967). (d) G. K. Helmkamp, H. N. Cassey, B. A. Olsen, and D. J. Pettitt, *J. Org. Chem.*, **30**, 933 (1965). (e) S. N. Nabi, S. Ahmad, and S. Ahmad, Jr., *J. Chem. Soc.*, 2636 (1963). (f) R. N. Haszeldine and J. M. Kidd, *ibid.*, 3219 (1953). (g) B. Milligan and J. M. Swan, *ibid.*, 2172 (1962).

(3) H. Fraenkel-Conrat, *J. Biol. Chem.*, **217**, 373 (1955).

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(5) B. T. Kaufman, *Proc. Nat. Acad. Sci. U. S.*, **56**, 695 (1966).

(6) D. M. Fawcett, *Can. J. Biochem.*, **44**, 1669 (1966).

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(8) (a) N. Kharasch, *J. Chem. Educ.*, **32**, 192 (1955). (b) F. Maloof and M. Soodak, *Pharmacol. Rev.*, **15**, 43 (1963).

(9) D. M. Fawcett, *Can. J. Biochem.*, **46**, 1433 (1968).

(10) L. Jirousek and L. W. Cunningham, *Biochim. Biophys. Acta*, **170**, 160 (1968).

(11) H. Rheinboldt and E. Motzkus, *Ber.*, **72B**, 657 (1939).

(12) J. A. Barltrop, P. M. Hayes, and M. Calvin, *J. Amer. Chem. Soc.*, **76**, 4348 1954).

(13) A. Fava, B. Reichenbach, and U. Peron, *ibid.*, **89**, 6696 (1967).

TABLE I

MOLAR EXTINCTION COEFFICIENTS (ϵ) OF $(CH_3)_3CSI$ (**3**) AT 444 AND 280 nm[a]

Procedure for synthesis of 3	No. of expts	Analytical technique (for substance determined)	Solvent[b]	ϵ_{444}	ϵ_{280}	Range[c] ϵ_{444}	ϵ_{280}	Yield, %[d]
A (2 added to I_2)	4	Uv (I_2)	M	64 ± 2	353 ± 8	4	18	53
		Titration (I_2)	M	68 ± 1	376 ± 9	4	22	51
		Photolysis,[e] then uv (I_2)	M	53 ± 0.3	...[f]	1.7		
		Photolysis,[e] then titration (I_2)	M	70 ± 13	...[f]	28		
B (I_2 added to 2)	4	Uv (I_2)	M	61 ± 9	345 ± 45	17	105	62
		Titration (I_2)	M	62 ± 2	350 ± 26	5	61	61
		Photolysis,[e] then uv (I_2)	M	41 ± 10	...[f]	27		
		Photolysis,[e] then titration (I_2)	M	58 ± 14	...[f]	33		
Average value for ϵ_{max} in M[g]				64	356			
C (eq 3, 5 + HI)	5	Nmr (3)	C	74 ± 8	...[b]	19		92
D (eq 4, 1 + ICl)	4	Nmr (3)	C	72 ± 6	...[b]	15		66
E (eq 5, 1 + I_2)	4	Nmr (3)	C	80 ± 5	...[b]	11		90
Average value for ϵ_{max} in C[g]				75				

[a] The ± values are standard deviations calculated as usual, $s = \sqrt{\Sigma d^2/(n-1)}$ (*cf.*, for example, D. A. Skoog and D. M. West, "Fundamentals of Analytical Chemistry," Holt, Rinehart, and Winston, New York, N. Y., 1963, p 47). "Titration" refers to the washing of an I_2 solution with excess $Na_2S_2O_3$ and back titration of the excess with aqueous I_2. [b] M, methylcyclohexane; C, carbon tetrachloride (chosen for its utility in nmr determinations; lack of uv transparency precluded determination of ϵ at 280 nm). [c] The range separating high and low values of the set. [d] Calculated as 100 (moles of **3** determined in the measurement of ϵ)/(theoretical moles of **3** possible); the highest yield observed by each method is reported. [e] Photolysis (eq 2) was followed by determination of I_2 from uv absorbance at 520 nm and by titration. [f] The λ_{max} at 280 nm disappeared upon photolysis, but **4** interfered too greatly for a reliable determination of ϵ. [g] A simple average of the values reported, disregarding standard deviations. Since photolyses were complex (see text), these values from procedures A and B were not included.
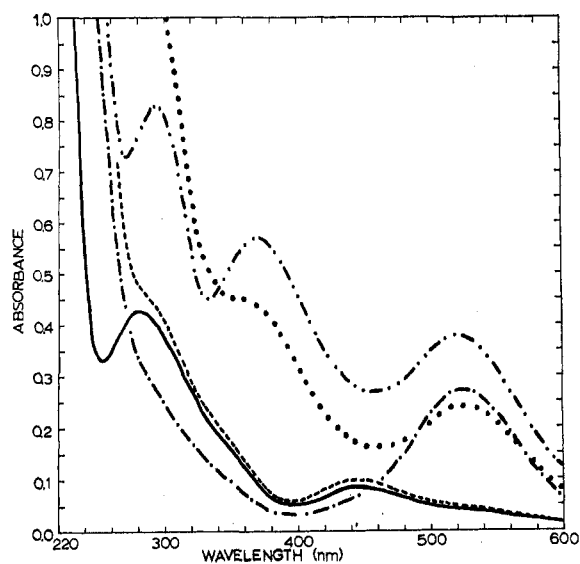

Figure 1.—Uv absorption spectra of **3**: in CCl_4 (0.0013 *M*), ------; in methylcyclohexane (0.0014 *M*), ———; in methylcyclohexane (0.0014 *M*) irradiated 5 min, —··—·· (this curve is essentially the summation of those for I_2 and **4**); irradiated 2 hr, —·—·; and irradiated 12 hr, ······.

Numerous preliminary experiments had established λ_{max} of **3** in methylcyclohexane at 444 nm (relatively little interference from **4** but a little from I_2) and at 280 nm (considerable interference from **4**). These features are reflected in Figure 1, prepared late in the study after such features became clear (it may help interpretation to add that one curve of Figure 1 closely resembles summation of those for I_2 and **4**; *cf.* legend). The absorbance of **3** at 444 nm and 280 nm after the wash, divided by the consumption of I_2 (assuming the amount of **3** equaled this consumption and remained unchanged), gave ϵ_{444} and ϵ_{280}; ϵ_{444} and ϵ_{280} thus could be calculated both from ϵ_{520} for I_2 ("Uv," Table I) and from the titrimetric analyses ("Titration," Table I).

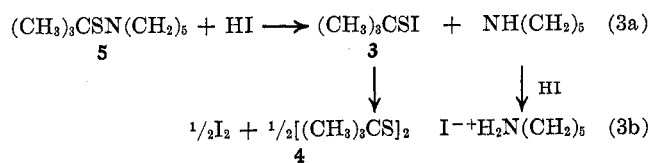*Brief* photolysis of **3** gave I_2, as shown by eq 2.

$$2(CH_3)_3CSI \xrightarrow{h\nu} [(CH_3)_3CS]_2 + I_2 \qquad (2)$$
$$\mathbf{3} \mathbf{4}$$
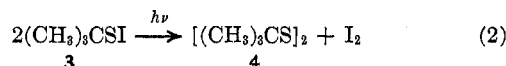
Analysis for I_2 both by uv and titration after photolysis of a solution of **3** of known absorbance permitted calculation of the third and fourth values shown for **3** under procedure A of Table I ("Photolysis"). These values were reassuring but (for reasons given later) were not included in the averages taken for ϵ.

In procedure B, the order of addition was reversed. There was no obvious difference in the reaction. Although the averages for ϵ_{444} and ϵ_{280} were slightly lower than by procedure A, they are considered reliable enough for inclusion in the average of all of the values, *i.e.*, ϵ_{444} 64 and ϵ_{280} 356 (Table I), which we suggest be used for solutions of **3** in methylcyclohexane. The lower values probably result from a favoring of the reaction of the salt **2** with **3** to form the disulfide **4** because of addition to excess **2**.

Procedure C was based on the reaction shown by eq 3a. Since eq 3 *in toto* provides a basis for iodometric determination of sulfenamides,[14] it seemed likely that the greater stability of **3** than of most sulfenyl iodides might permit the reaction of **5** to be stopped in its first phase, eq 3a. The realization of this possibility led to

$$(CH_3)_3CSN(CH_2)_5 + HI \longrightarrow (CH_3)_3CSI + NH(CH_2)_5 \qquad (3a)$$
$$\mathbf{5} \mathbf{3}$$

$$\downarrow \downarrow HI$$

$$^{1}/_{2}I_2 + {}^{1}/_{2}[(CH_3)_3CS]_2 \quad I^{-+}H_2N(CH_2)_5 \qquad (3b)$$
$$\mathbf{4}$$

procedure C. As can be seen from Figure 1, use of carbon tetrachloride as a solvent precludes observation of ϵ_{max} at 280 nm. The most convenient determination of ϵ_{444} proved to be by washing out of piperidinium and iodide ions and evaluation of the concentration of **3** by nmr with an internal standard (**3** shows a sharp singlet

(14) W. Groebel, *Chem. Ber.*, **92**, 2887 (1959).

at δ 1.45, well separated from that of either the sulfenamide **5** at δ 1.18 or the disulfide **4** at δ 1.30). Concentrations were varied in procedure C over a sevenfold range in the evaluation of ϵ_{444} shown in Table I (similar variations in concentration were made in the other procedures to broaden the basis for ϵ). Photolysis of **3** in procedure C unfortunately could not be used to check ϵ_{444} presumably because of interfering reactions of trace contaminants. Rheinboldt and Mott used a variation of procedure C to prepare 2-methyl-2-propanesulfenyl bromide and chloride but not **3**.[15] By procedure C, **3** was prepared in high yield but seldom was the nmr spectrum of the **3** virtually free of the disulfide **4**. At first, procedure C seemed to be an attractive path to **3** but a study as **3** decomposed indicated otherwise. In the presence of $\sim$10% of the unconverted **5**, and possibly of other trace impurities, the washed solution soon showed a variety of products, and the final yield of *t*-butyl trisulfide was as great as that of the disulfide **4**.

Procedure D was based on eq 4. A slight excess of iodine monochloride was used to assure complete conversion of **1** and then was destroyed with thiosulfate. Procedure D was more difficult to control than the others. The quantities of initial reactants and the time of mixing were critical. Too long a reaction time or too great an excess of ICl carried the final products well beyond **3**. The nmr spectrum of the solution

$$(CH_3)_3CSH + ICl \longrightarrow (CH_3)_3CSI + HCl \qquad (4)$$
$$\quad\;\; 1 \qquad\qquad\qquad\quad 3$$
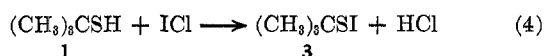
ordinarily obtained gave five sharp singlets; these are attributed to **1, 3, 4**, *t*-butyl trisulfide, and an unknown.

Procedure E perhaps is the most satisfying preparative route for **3**. It was based on eq 5, which it will be recalled was mentioned earlier without elaboration.[12] Thiol **1** in carbon tetrachloride was added to excess I_2

$$(CH_3)_3CSH + I_2 \longrightarrow (CH_3)_3CSI + HI \qquad (5)$$
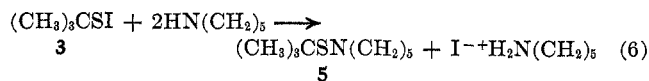$$\quad\;\; 1 \qquad\qquad\qquad 3$$
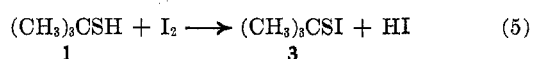
in the presence of water. The solution was washed with aqueous thiosulfate and water, operations which proved to be the key to the success of procedure E. The thiol was converted completely to a solution of sulfenyl iodide **3** containing some disulfide **4** (a minimum of $\sim$16% by nmr). Since little reaction reportedly occurs between many thiols and iodine in nonpolar solvents even upon heating,[13,16] the presence of water presumably explains the success of procedure E. The extinction coefficient of **3** was evaluated using nmr as in procedures C and D (Table I; see Experimental Section). The average of all values from procedures C, D, and E gave ϵ_{444} 75, the value suggested for use with **3** in CCl$_4$.

In procedures A–E, one must be wary of charge transfer complexes involving combinations of **1, 3, 4**, and I_2. For example, I_2 and **4** show an absorption peak at 328 nm in methylcyclohexane and a shoulder at $\sim$333 nm in CCl$_4$ (neither are seen in the spectra of I_2 or **4**), and λ_{max} for I_2 is shifted slightly low from $\sim$520 nm; a charge transfer band has not been reported for I_2 with **4** but has been for I_2 with other disulfides,[17] as well as with

thiols.[17a] Species such as triiodide ion,[18] especially in procedure E (eq 5), probably also are involved in the *initial* reaction mixture. The **3** evidently does not form complexes with iodide or iodine, however; thus its solution was not changed when stirred with aqueous potassium iodide (poor distribution of the potassium iodide into CCl$_4$ presumably is not responsible, since $Na_2S_2O_3$ reacted readily under similar conditions; *vide infra*); similarly, when I_2 was added to **3**, the spectrum simply was the sum of the two and a sodium thiosulfate wash left only **3**. The wash of aqueous thiosulfate and then water in procedures A–E *before* determination of ϵ for **3** presumably removed any charge transfer species, so that the ϵ values reported for **3** should be those of **3** and not of other species; reasonable agreement of the ϵ values obtained by the numerous methods of Table I support this conclusion, as does other evidence for the presence of **3** (*vide infra*).

Reactions.—As mentioned, photolysis of **3** provided a reassuring check on the presence of **3**. Beforehand, however, we had encountered a report that trifluoromethanesulfenyl chloride forms from the disulfide and chlorine upon uv irradiation;[2f] furthermore, Barltrop, Hayes, and Calvin felt that the disulfide **4** was cleaved to **3** by I_2.[12] It therefore seemed wise to check the possibility that light might effect for I_2 the type of cleavage of disulfides which is well known to give sulfenyl chlorides under ordinary conditions with chlorine. Uv irradiation of a solution of I_2 and **4** produced no absorption at 280 or 444 nm which would indicate formation of **3**; I_2 appeared to be consumed and triiodide ion to be formed (appearance of two new absorptions at 288 and 362 nm; *cf.* ref 18). Indeed, as Figure 1 shows and more in accord with expectation, when **3** was irradiated for 5 min, its two characteristic absorbances disappeared and I_2 was released (new absorption at 520 nm; eq 2). After *ca.* 2 hr more, this absorption increased by $\sim$30%, and two new peaks appeared consistent with triiodide formation. These changes are shown in Figure 1. The photolytic decomposition of **3** (eq 2) was zero order (*cf.* Figure 2), with the rate of decomposition of **3** (-0.0019 mequiv/min by loss of absorbance at 280 or 444 nm) being virtually the same as the rate of formation of I_2 ($+0.0011$ mequiv/min by titration with thiosulfate; $+0.0019$ mequiv/min by cumulative absorption at 520 nm). After $\sim$50–60% of **3** had decomposed, the complexity of the reaction increased, as reflected by the change in slope of two of the curves in Figure 2, perhaps because accumulating byproducts began to consume I_2 or because accumulated **4** reduced uv absorption by the solution.

Rheinboldt and Motzkus demonstrated the identity of **3** by converting it to sulfenamides with amines.[11] Since we had had experience with N-(*t*-butylthio)-piperidine (**5**),[19] early in our work we confirmed the identity of **3** (from procedure B) by converting it to **5** (90% yield; eq 6); uv and nmr spectra showed that the appearance of **5** corresponded to the disappearance of **3**.

$$(CH_3)_3CSI + 2HN(CH_2)_5 \longrightarrow$$
$$\;\; 3$$
$$\qquad\qquad (CH_3)_3CSN(CH_2)_5 + I^{-+}H_2N(CH_2)_5 \qquad (6)$$
$$\qquad\qquad\qquad\qquad\qquad\quad 5$$

(15) H. Rheinboldt and F. Mott, *Ber.*, **72**, 668 (1939).

(16) E. C. Kooyman, "Organosulfur Chemistry," M. J. Janssen, Ed., Interscience, New York, N. Y., 1967, p 6.

(17) (a) M. Good, A. Major, J. Nag-Chaudhuri, and S. P. McGlynn, *J. Amer. Chem. Soc.*, **83**, 4329 (1961). (b) H. Tsubomura and R. P. Lang, *ibid.*, **83**, 2085 (1961). (c) B. Nelander, *Acta Chem. Scand.*, **20**, 2289 (1966).

(18) (a) A. D. Awtrey and R. E. Connick, *J. Amer. Chem. Soc.*, **73**, 1842 (1951). (b) L. I. Katzin, *J. Chem. Phys.*, **21**, 490 (1953).

(19) (a) N. E. Heimer and L. Field, *J. Org. Chem.*, **35**, 3012 (1970). (b) We thank Dr. Heimer for several helpful suggestions.
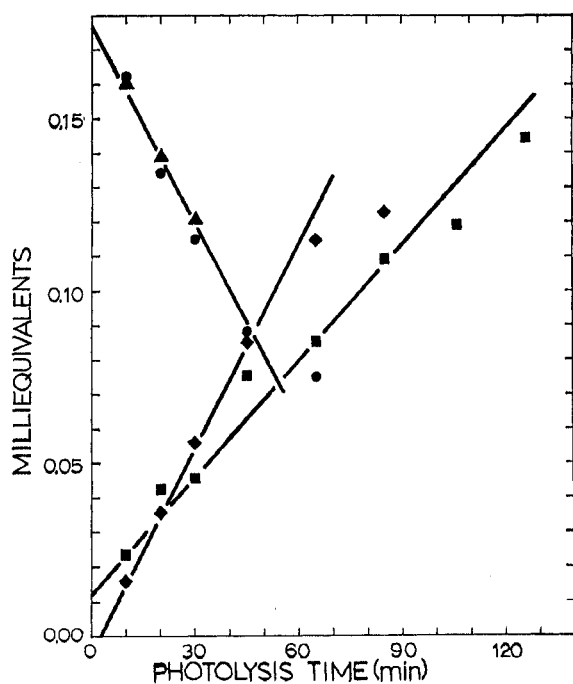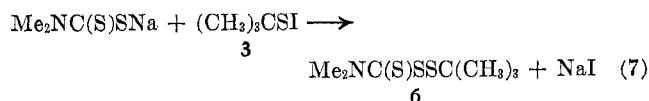
Figure 2.—Photolysis study of 3 (0.17 mequiv): ●, mequiv of 3 remaining as determined by A_{444} (slope, -0.0019 mequiv/min); ▲, mequiv of 3 remaining as determined by A_{280} (slope, -0.0019 mequiv/min); ■, cumulative mequiv of I_2 released as determined by titration (slope, $+0.0011$ mequiv/min); ◆, cumulative mequiv of I_2 released as determined by A_{520} (slope, $+0.0019$ mequiv/min).

Further confirmation was obtained by converting 3 to the known unsymmetrical disulfide 6 of eq 7 (27% yield).

$$Me_2NC(S)SNa + (CH_3)_3CSI \longrightarrow$$
$$\qquad\qquad 3$$
$$\qquad\qquad Me_2NC(S)SSC(CH_3)_3 + NaI \quad (7)$$
$$\qquad\qquad\qquad 6$$

Some reactions failed or were unpromising. In testing for the possible use with sulfenyl iodides of a method used to determine sulfenyl chlorides,[20] 3 in methylcyclohexane was added to potassium iodide in acetic acid. Addition of thiosulfate (to measure I_2) and back-titration with I_2 showed that the 3 did not decompose immediately to I_2. Longer contact times still were inconclusive; indeed, back-titration of the thiosulfate required more standard I_2 than had the thiosulfate initially.

Evidence for the identity of 3 now can be summarized. (a) Procedures A–E gave 3 with essentially the same features in the uv spectrum and with ϵ values in reasonable agreement, including values based on photolysis of 3 to I_2 and the disulfide 4, a reaction which itself supports the structure. (b) Nmr spectra of solutions of 3 (procedure A) showed only two peaks, one being from 3 and the other from 4; as the spectrum of 3 disappeared, that of 4 increased. Nmr spectra of solutions obtained by the other procedures all were understandable in these terms, although other substances were present. (c) Two known derivatives were prepared from 3; with one (5, 90% yield), the uv and nmr absorptions of 3 disappeared as those of 5 appeared.

Reactivity and Stability.—Rheinboldt and Motzkus made a few qualitative observations on the behavior of 3 in ether.[11] We have extended these more quanti-
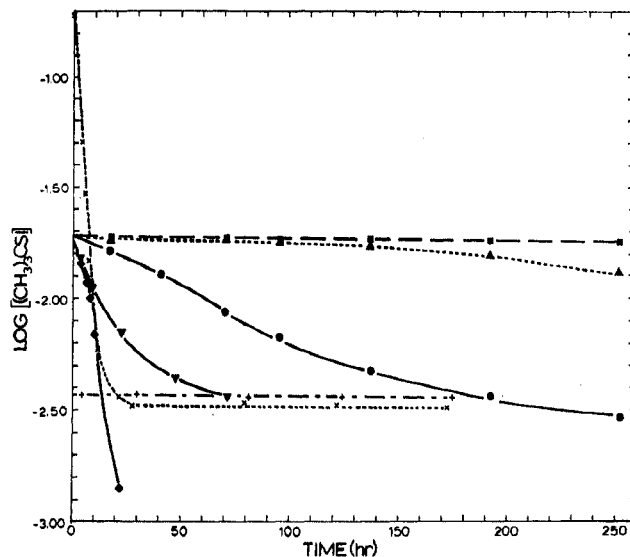
(20) N. Kharasch and M. M. Wald, *Anal. Chem.*, **27**, 996 (1955).

Figure 3.—Reactivity and stability of 3 (original molarity indicated on the vertical axis): ●, ambient conditions; ▲, dark, $\sim 25°$; ■, dark $\sim -12°$; ◆, stirred with 0.1 N $Na_2S_2O_3$; ▼, stirred with 0.1 N KI_3; x, concentrated solution (0.19 M); +, diluted solution (0.004 M) (the latter two at 25° in the dark).

tatively. Portions of a solution of 3 in CCl_4 first were subjected to varying conditions of light and temperature. The results are shown in Figure 3. The survival time for 50% of the 0.019 M 3 stored under ambient conditions was nearly 3 days. In the dark, 67% survived after 11 days, however, and when a dark sample also was kept cold ($-12°$) nearly all survived.

In an assessment of effects of reagents, when water or aqueous 0.1 N potassium iodide was stirred in contact with portions of a 0.018 M solution in carbon tetrachloride (dark, $\sim 25\%$), the survival of 3 was essentially the same as above. However, stirring with 0.1 N sodium thiosulfate and 0.1 N potassium triiodide resulted in 50% survival times of 9 and 15 hr, respectively (Figure 3). The results with sodium thiosulfate should have negligible relevance to those in determining ϵ_{max}, where only 0.05 N sodium thiosulfate was used and where contact was for only 1 min, although they suggest the inapplicability of the sodium thiosulfate-wash technique for determining ϵ_{max} of sulfenyl iodides much more reactive than 3. The reaction of 3 with potassium triiodide suggests that procedure E might be improved for preparative use by minimizing the excess of I_2, although not for determination of ϵ_{max} where the singlet of 1 (δ 1.42) might complicate use of that of 3 (δ 1.45).

Figure 3 also illustrates the effect of the concentration of 3 on its stability. The 50% survival time of a 0.2 M solution of 3 (among the most concentrated used) in the dark at 25° was only 3.5 hr. In marked contrast, a 0.004 M solution was largely unchanged after 7 days, suggesting that sulfenyl iodide moieties on proteins may exist, at least in part, because of very low effective concentration, amounting almost to isolation.

Structural effects on reactivity were considered also (although only in a preliminary way), since the relatively low reactivity of 3 has been attributed to a neopentyl-type steric hindrance on the sulfur atom of 3, which opposes back-side attack by nucleophiles.[16] The tertiary structure of 3 did indeed prove to be a

special case, since the silver thiolates of 1-butane- or 2-butanethiol showed no tendency to form stable sulfenyl iodides (procedure A); thus no product resulted which showed uv absorption near 440 nm or which liberated I_2 on photolysis. On the other hand, triphenylmethanethiol in procedure E showed in the 320–600-nm range a λ_{max} at 440 nm (only); photolysis and titration of I_2 formed indicated a yield of sulfenyl iodide of at least 70%.

Experimental Section[21]

Materials.—Methylcyclohexane, CCl_4, and 1,4-dioxane were Matheson Coleman and Bell Spectroquality reagents. "Baker Analyzed" ACS-grade I_2 was used. The **1** was a practical grade (97%); its nmr spectrum in CCl_4 showed it to be free of **4**. Practical grade **4** was redistilled in a 0.5 × 60 cm Nester–Faust annular column, n^{25}D 1.4863 (lit.[23] n^{20}D 1.4899); glpc showed the distillate to be pure; it was stored in the dark under N_2. Silver 2-methyl-2-propanethiolate (**2**) was prepared fresh for each experiment as reported;[24] it was dried at 0.1 mm overnight. Iodine monochloride[25] was distilled, bp 97–105°.[26]

Preparations and Molar Extinction Coefficients (ϵ) of 2-Methyl-2-propanesulfenyl Iodide (3). A. By Addition of 2 to I_2.—A typical experiment on which the values of Table I are based was as follows. A solution 0.00956 M in I_2 in methylcyclohexane was prepared (ϵ_{520} 935). The thiolate **2** (0.990 mmol) was added to 75.00 ml (0.717 mmol) of this solution at ~0° in a glass-stoppered flask. The mixture was shaken for 1 min; then AgI was removed using a sintered-glass funnel.

For the determination of ϵ by "Titration (I_2)" (Table I), the temperature of the filtrate was allowed to rise to ~25°, and a 20.00-ml aliquot was shaken with 0.0612 N $Na_2S_2O_3$ (10.00 ml), then twice with water; the washings were combined and titrated with 0.0507 N KI_3 (8.09 ml); on the assumption that all I_2 used gave **3**, from the absorbances (A_{444} 0.310, A_{280} 1.707) ϵ_{444} and ϵ_{280}, respectively, then were calculated: $(0.310)(75.00)/[0.717 - (0.612 - 0.410)(0.5)(75/20)] = 68.7$ and $(1.707)(75.00)/[0.717 - (0.612 - 0.410)(0.5)(75/20)] = 378.5$. The average of four such experiments gave the values of 68 ± 1 (ϵ_{444}) and 376 ± 9 (ϵ_{280}) in Table I. Such solutions of **3** were orange-red with sharp, lachrymatory odors. The highest yield of the four samples, 51%, is reported in Table I. The yield for the foregoing typical sample, for example, was calculated as follows: $[0.717 - (0.612 - 0.410)(0.5)(75/20)](100)/(0.717) = 47\%$.

For the determination of ϵ by "Uv (I_2)" (Table I), uv spectra of the same aliquot before the wash showed the absorbance (A) at 520 nm to be 4.647 (0.641 corrected for dilution of 0.40 to 2.90 ml) and after the wash to be 0.151 (slight tailing from A_{444} of **3**). The amount of residual I_2 after its reaction with **2** therefore was $(4.647 - 0.151)/935 = 0.00481$ M, and ϵ_{444} thus was 65.3 $[0.310/(0.717/75 - 0.00481 = 0.00475)]$; similarly,

ϵ_{280} was 359.3. The average for four such experiments gave the values 64 ± 2 (ϵ_{444}) and 353 ± 8 (ϵ_{280}) in Table I. The highest yield of the four samples, 53%, is reported in Table I. The yield for the foregoing typical sample was calculated as $(0.00475)(100)/(0.717/75) = 50\%$.

In the analysis by "Photolysis" (Table I), the preferred alternative of determining ϵ_{444} for **3** simply by dividing A_{444} for a solution by twice the moles of I_2 produced on photolysis was precluded by side reactions after about 50–60% completion. Hence ϵ, "Photolysis, then titration (I_2)" (Table I), was determined by dividing A for a solution of **3** *after* photolysis by the calculated concentration of **3** remaining *after* photolysis, as follows: The remaining 55 ml of the solution of **3** was washed like the first portion and combined with it. The 75 ml then was photolyzed (the temperature rose to ~100°) for 5.0 min (optimum time established beforehand) in a quartz flask fitted with a reflux condenser. A 20.00-ml aliquot, at ~25°, was washed with 10.00 ml of 0.0612 N $Na_2S_2O_3$ (0.612 mequiv) and H_2O; the combined washings were titrated with 11.03 ml of 0.0507 N KI_3 (0.559 mequiv); the amount of I_2 formed, hence of **3** decomposed, was $(0.612 - 0.559)(75/20) = 0.198$ mequiv (59% decomposed). Residual **3** in the 75.00 ml thus was $[0.717 - (0.612 - 0.410)(0.5)(75/20)] - 0.198 = 0.140$ mmol, *i.e.*, corresponding to a solution 0.00187 M in **3**. The A_{444} of this remaining **3** was 0.120; hence $\epsilon_{444} = 64.2$. The value of ϵ_{444} 70 ± 13 (Table I) was an average of four such experiments.

Uv spectra of the 75 ml were taken before and after the wash which followed photolysis to determine ["Photolysis, then uv (I_2)"; Table I] the amount of I_2 liberated and, from this, of undecomposed **3**. A's of the solution at 520 nm before and after washing were 1.233 and 0.060, respectively; hence the amount of **3** which survived left a 0.00225 M solution $[0.00475 - 2 (1.233 - 0.060)/935 = 0.00250]$; therefore ϵ_{444} was $0.120/0.00225 = 53.3$. The value of 53 ± 0.3 (ϵ_{444}) in Table I was an average of photolysis results on the four samples used in the other techniques.

A control containing 0.358 mmol of I_2 in 25 ml of methylcyclohexane was photolyzed for 10 min. Titration of a photolyzed aliquot as above showed essentially no change (0.364 mmol) in the concentration of I_2. Uv spectra at 520 nm after this photolysis indicated the amount of I_2 was 0.357 mmol.

B. Addition of I_2 to 2.—A solution 0.01434 M in I_2 in methylcyclohexane was prepared. The procedure was essentially that of A except that a known quantity of the I_2 solution at 0° was added in one portion to the thiolate in the proportions used in A. The same procedure was followed as in A for analysis of ϵ_{444} and ϵ_{280}. The average values for procedure B listed in Table I also represent four experiments.

C. Cleavage of N-(t-Butylthio)piperidine (5).—As was outlined for **5**,[27] disulfide **4** (0.1 mol) was chlorinated in petroleum ether with 0.1 mol of Cl_2 at approximately 25°. This solution was added to 0.4 mol of piperidine in petroleum ether and 0.4 mol of NaOH in H_2O during 30 min. The organic layer was washed with H_2O, dried (Na_2SO_4), and evaporated. Distillation (200-mm Vigreux column) gave colorless **5**: 21.0 g (61%); n^{24}D 1.4750, lit.[27b] n^{20}D 1.4765; nmr (CCl_4) δ 1.18 (s). No **4** was observed (δ 1.30, s).

A typical cleavage was as follows: 15.0 ml of 0.2 M aqueous HI (3 mmol) was added to 224 mg (1.3 mmol) of **5** in 15 ml of CCl_4 (0.09 M solution), and the mixture was shaken vigorously for 2 min (concentrations of the **5** were varied in five experiments from 0.03–0.2 M, with proportional changes in the amount of HI used).

The organic layer was washed twice with H_2O, twice with 0.05 N $Na_2S_2O_3$, then twice again with H_2O; the uv spectrum was typical of **3** with A_{444} 5.643 (calculated from the observed A of 0.513, after dilution of 0.25 to 2.75 ml). The concentration of **3** was determined immediately by placing 10.0 μl of dioxane (0.117 mmol) in an nmr tube with 1.00 ml of the washed solution. The peak areas of the resulting singlets of 4.73 for the 8 protons of dioxane (δ 3.57) and of 3.60 for the 9 protons of **3** (δ 1.45) indicated, since an equimolar amount (*i.e.*, 0.117 mmol) of **3** should have an area of 5.32, that 0.0792 mmol $[i.e., (3.60/5.32)(0.117)]$ of **3** was present in the volume of 1.01 ml of solution. The molar concentration of **3** thus was 0.0784 M and ϵ_{444} was 71.9 (*i.e.*, 5.643/0.0784). The value of 74 ± 8 (Table I) is the average of

(21) Uv spectra were obtained using matched 10-mm standard silica cells with a Beckman Model DB recording spectrophotometer; photometric accuracy was checked weekly with a K_2CrO_4 solution;[22] we are much indebted to Professor T. M. Harris for the use of this instrument. Nmr spectra were obtained with a Varian Model A-60 (TMS as internal standard). Mass spectra were kindly determined by C. T. Wetter using an LKB Model 9000 instrument (70 eV, gc inlet), obtained through NSF Science Development Program Grant GU-2057; only parent peaks and those exceeding 5% in relative intensity at m/e >40 are reported. Unless otherwise stated, reactions were done at ~25°, and irradiations were done in a quartz vessel 5 cm from a Hanovia 100-W uv lamp. Glpc measurements were done on a Varian Aerograph instrument using an SE-30 column (3%, 0.6 × 150 cm, 100–120 mesh Chromosorb P). Standard solutions were checked weekly; aqueous KI_3 was standardized against As_2O_3 (99.99% assay, G. Frederick Smith Chemical Co.) and $Na_2S_2O_3$ against the KI_3; solutions of I_2 were standardized by washing aliquots with $Na_2S_2O_3$, then H_2O, combining the washes, and using KI_3; "Vitex" (a modified amylose; G. Frederick Smith Co.) was the indicator. Melting points are corrected.

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(23) J. H. Karchmer in "Treatise on Analytical Chemistry," Part II, Vol. 13, I. M. Kolthoff and P. J. Elving, Ed., Interscience, New York, N. Y., 1966, p 366.

(24) *Cf.* ref 18 in T. F. Parsons, J. D. Buckman, D. E. Pearson, and L. Field, *J. Org. Chem.*, **30**, 1923 (1965).

(25) J. Cornog and R. A. Karges, "*Inorg. Syn.*," **1**, 165 (1939).

(26) G. H. Woollett and W. W. Johnson in "Organic Syntheses," Coll. Vol. II, A. H. Blatt, Ed., Wiley, New York, N. Y., 1947, p 344.

(27) (a) C. M. Himel, U. S. Patent 2,807,615 (1957); *Chem. Abstr.*, **52**, 14706 (1958). (b) C. M. Himel and L. O. Edmonds, U. S. Patent 2,520,400; *Chem. Abstr.*, **44**, 10735 (1950).

five such experiments. The chemical shift of the methyl groups of **3** (δ 1.45, s), made this determination possible, since it differed from those of **5** (δ 1.18, s), **4** (δ 1.30, s), or **1** (δ 1.42, s).

Photolysis as a check of the value of ϵ_{444} was inconclusive; no I_2 was liberated, the solution became dark brown (unchanged by $Na_2S_2O_3$), and solid precipitated; trace contaminants (*e.g.*, piperidine or HI) probably led to further reactions of I_2.

D. Addition of ICl to 1.—A solution of 0.728 g (4.49 mmol) of ICl in 7 ml of CCl_4 was added to one of 0.320 g (3.55 mmol) of **1** in 16 ml of CCl_4 in a separatory funnel. The mixture was shaken for 1 min and then was washed immediately three times with H_2O, with 0.05 N $Na_2S_2O_3$ until the color remained constant, and then again three times with H_2O. The discernible part of the uv spectrum was identical with that of **3** prepared as in A. The ϵ_{444} of **3** was determined by uv and nmr (dioxane as an internal standard) as in C. Nmr chemical shifts, assignment, and per cent of total peak area, respectively, for the five singlets observed with a typical product were δ 1.30, **4**, 5;[28] δ 1.37, *t*-bu-S_3-*t*-bu, 13;[28] δ 1.42, **1**, 4; δ 1.45, **3**, 69; and δ 1.60, unknown, 10. After 2 days in the nmr tube under ambient conditions only sharp singlets at δ 1.30, 1.37, and 1.60 remained; the relative intensity of δ 1.30 increased tremendously, and I_2 was released.

E. Addition of 1 to Excess I_2.—A 0.095 M solution of **1** (30.00 ml, 2.85 mmol) in CCl_4 was poured into a glass-stoppered flask containing 10 g (39.4 mmol) of solid I_2. Water (20 ml) was quickly added, and the mixture was shaken vigorously for 5 min. The organic layer was filtered (sintered glass), washed with H_2O twice, with 0.05 N $Na_2S_2O_3$ until the color was constant, then three times more with H_2O; ϵ_{444} was determined by uv-nmr as in C.

Reactions of 3. A. Photolysis.—In the preliminary study (see Discussion), a solution 0.0003 M in both **4** and I_2 in methylcyclohexane was irradiated. The uv spectrum was compared periodically with spectra of separate control solutions of I_2 and **4**. No indication of the characteristic absorption of **3** (280, 444 nm) could be seen. It was soon found that **3** from procedure B ($\sim$0.002 N) when thus irradiated decomposed immediately (*cf.* Figure 1 and Discussion).

The results plotted in Figure 2 were obtained as follows. A suspension of **2** (101.7 mg, 0.516 mmol) in 16 ml of methylcyclohexane was chilled with Dry Ice in a foil-covered centrifuge tube capped with a rubber septum, and a solution of I_2 (25 ml, 0.0208 N, 0.520 mequiv) at 5° was introduced with a syringe. The contents were shaken vigorously for 1.5–2.0 min and centrifuged. The supernatant liquid was immediately removed, the uv spectrum was taken, and the liquid was washed with 0.0606 N $Na_2S_2O_3$ (10.00 ml, 0.606 mequiv) and water. The combined washings were titrated against 0.0505 N KI_3 (8.70 ml, 0.439 mequiv); hence the amount of **3** in the 41.00 ml of solution was 0.176 mmol [(0.520 − 0.167)/2], and the molarity of **3** was 0.0043. The washed solution then was irradiated (*15 cm from the lamp instead of the usual 5*). Periodically, the entire solution (to minimize I_2 absorption) was removed and washed free of I_2 with 10.00-ml aliquots of 0.0606 N $Na_2S_2O_3$, which were titrated against 0.0505 N KI_3 to determine the amount of I_2 released. Uv spectra were taken before and after each wash to determine both the quantity of I_2 released and A at 444 and 280 nm for calculation of **3** surviving. Figure 2 shows the results from both the spectrophotometric and titrimetic analyses of I_2 released, and the remaining concentration of **3** as followed by decrease in A at 444 and 280 nm.

B. With Piperidine.—A solution of **3** prepared (procedure B) by adding 0.027 mol of I_2 in CCl_4 (5°) to 0.076 mol of pulverized **2** in CCl_4 (5°), shaking for 1 min, filtering, and washing with $Na_2S_2O_3$ solution and then with water was added over 1 hr to piperidine (0.1 mol) in CCl_4 and 160 ml of aqueous 0.1 N buffer (pH 7). Nmr spectra of the CCl_4 solution taken initially, when one-half of the **3** had been added, and at the end of the addition showed the sharp singlet of **3** (δ 1.45) disappearing as the sharp singlet of **5** (δ 1.18) appeared. Uv spectra of the initial solution showed the characteristic absorption of **3** (λ_{max} 444 nm), but uv spectra of the final solution showed no λ_{max}, only end absorption. The organic layer was washed twice with H_2O and dried (Na_2SO_4). Evaporation of solvent left 4.2 g of yellow-orange liquid (90%, calcd as **5**). Glpc indicated the liquid to be virtually pure by comparison with retention times and areas of **4** and authentic

N-(*t*-butylthio)piperidine (**5**),[19a,29] n^{28}D 1.4759 (lit.[27b] n^{20}D 1.4765); only the boiling point of **5** was reported by Rheinboldt and Motzkus.[11] The mass spectrum was essentially identical with that of authentic **5**.[19a,29]

C. With Sodium N,N-Dimethyldithiocarbamate.—According to procedure B, 475 ml of 0.142 M I_2 (67.4 mmol) in methylcyclohexane was added in one portion to 21 g (106.6 mmol) of **2** with vigorous stirring below −20°. Solid was removed, and the filtrate was added at $\sim$25° (1 hr) to 20 g (140 mmol) of sodium N,N-dimethyldithiocarbamate in 150 ml of H_2O. The mixture was stirred overnight, and the organic layer was washed with H_2O and evaporated. Recrystallization of the residue from MeOH (Dry-Ice cooling) gave 3.75 g (27%) of *t*-butyl N,N-dimethyltrithiopercarbamate (**6**), mp and mmp 70–71°, lit.[30] mp 70–71°; the ir and nmr spectra were identical with those of authentic **6**.[30]

Stability and Reactivity of 3. A. Effect of Ambient Light and Temperature.—A solution of 1.0 ml ($\sim$0.01 mol) of **1** in CCl_4 (500 ml) was added (procedure E) to I_2 (10 g, 0.04 mol) and H_2O (100 ml). The mixture was stirred (5 min), filtered, and washed free of I_2 as usual. The concentration of **3** (from A_{444} 1.41, assuming ϵ_{444} 75) was 0.0188 M. The solution was placed in three glass-stoppered Pyrex flasks. One (foil-wrapped) flask was stored at −12°; another (foil-wrapped) was stored at $\sim$25°; the third was stored at $\sim$25° in ambient light. Periodically, samples from each were washed with 0.05 N $Na_2S_2O_3$ and water; A_{444} was obtained to determine the concentration of **3**. Figure 3 records the results.

B. Effect of Reagents.—A solution like that in part A (but 0.0180 M in **3**) was divided into four 100-ml portions, stored in the dark, and vigorously stirred respectively with 100 ml of H_2O, 100 ml of 0.1 N KI, 100 ml of 0.1 N KI_3, and 100 ml of 0.1 N $Na_2S_2O_3$. Samples taken periodically from each were washed with 0.05 N $Na_2S_2O_3$ and H_2O (H_2O alone for the solution with the $Na_2S_2O_3$); the concentration of **3** then was determined from A_{444}, with the results shown in Figure 3 for $Na_2S_2O_3$ and KI_3. The H_2O and KI effected no significant change during the period of study.

C. Effect of Concentration.—Part of a solution like that in part A (but 0.192 M in **3**) was diluted to 0.0036 M ($\sim$53-fold, necessitating the use of "Log [(CH₃)₃CSI]" for Figure 3). The original and diluted solutions were stored in the dark at $\sim$25° in glass-stoppered flasks. The concentration of **3** was followed by washing samples periodically with 0.05 N $Na_2S_2O_3$ and H_2O and observing A_{444}, with the results shown in Figure 3.

D. Structural Considerations. 1. Attempted Synthesis of 1-Butanesulfenyl Iodide and 2-Butanesulfenyl Iodide.—Silver 1-butanethiolate and 2-butanethiolate were prepared fresh by adding $NaOAc \cdot 3H_2O$ (6.7 g, 0.05 mol) and the thiol (4.9 g, 0.05 mol) in H_2O (25 ml) to $AgNO_3$ (8.5 g, 0.05 mol) in H_2O (25 ml); the precipitates were washed with H_2O, EtOH, and Et_2O and then were dried at 0.1 mm overnight. To 10.00 ml of 0.0298 N I_2 (0.298 mequiv) in methylcyclohexane in a foil-covered centrifuge tube, capped with a rubber septum, and cooled in Dry Ice there was added 0.1122 g (0.569 mmol; the excess was used to minimize residual I_2, which would interfere with later measurements) of silver 1-butanethiolate (procedure A). The contents were shaken 1 min and centrifuged. The supernatant liquid was withdrawn immediately (purple, presumably indicating some unreacted I_2). Without the usual contact with $Na_2S_2O_3$ or H_2O, the solution was quickly diluted and analyzed by uv. Only λ_{max} 520 nm (for I_2) was observed (A 1.620). The cuvette then was irradiated for 5 min; the uv spectrum then still showed only a λ_{max} for I_2 (A_{520} 1.332). Since the absorbance of I_2 did not increase upon irradiation, as is characteristic of **3**, 1-butanesulfenyl iodide seems unlikely to have been present. Furthermore, when some of the initial solution was washed with $Na_2S_2O_3$, color was completely removed (similar solutions of **3** were orange-red). When the time of reaction was extended to allow all I_2 just to be consumed ($\sim$2 min), the supernatant solution was completely colorless and irradiation had no effect. Identical results were obtained with 0.1012 g (0.514 mmol) of silver 2-butanethiolate.

2. Triphenylmethanesulfenyl Iodide.—Triphenylmethanethiol (2.00 g, 7.25 mmol) in 125 ml of CCl_4 was added ($\sim$25°) to 10 g (40 mmol) of I_2 and 75 ml of H_2O. The mixture was shaken for 3 min, washed twice with 0.1 N $Na_2S_2O_3$, and twice with H_2O.

(28) L. Field and W. B. Lacefield, *J. Org. Chem.*, **31**, 3555 (1966): **4**, τ 8.65 (s); (CH₃)₃CSSSC(CH₃)₃, τ 8.55 (s); solvent not stated.

(29) We thank Dr. N. E. Heimer for a sample of **5**.

(30) L. Field and J. D. Buckman, *ibid.*, **33**, 3865 (1968).

The uv spectrum showed a λ_{max} of 440 nm (only, except for the typical end absorption of **3** in CCl₄, Figure 1) with A_{440} being 6.784 (0.424, corrected for dilution of 0.20 to 3.20 ml). The entire 125-ml solution was photolyzed in a quartz flask attached to a reflux condenser for 20 min. Appearance of a new λ_{max} at 520 nm indicated formation of I₂. A 10.00-ml aliquot of the resulting solution was washed with 15.00 ml of 0.0559 N Na₂S₂O₃, which then consumed 8.52 ml of 0.0508 N KI₃, indicating the formation

of 5 mequiv of I₂ presumably from 5 mequiv of sulfenyl iodide (yield, at least ~70%).

# Coupling, Carbonylation, and Vinylation Reactions of Aromatic Sulfinic Acids *via* Organopalladium Intermediates

KLAUS GARVES

E. I. du Pont de Nemours and Company, Experimental Station, Explosives Department, Wilmington, Delaware 19898

The expulsion of sulfur dioxide from arenesulfinic acids and their salts by palladous salts in a variety of solvents is reported. The aryl groups couple to form a biaryl in 35% yield, and Pd²⁺ is reduced to metallic palladium. Mercuric chloride acts as a catalyst and doubles the yield of the biaryl. The reaction presumably proceeds by formation of an arylpalladium complex. In the presence of carbon monoxide, olefins, or nitriles insertion reactions take place leading to carbonylation, vinylation, or acylation of arenesulfinate anions in low to medium yields.

Recently the formation of arylpalladium complexes from arylmercuric chloride and palladium chloride was postulated.[1] Owing to the low stability of the organometallic intermediate only the products of subsequent reactions, biaryls and palladium metal or insertion products in the presence of CO or olefins, were isolated. Likewise, benzeneboronic acid and palladium acetate yielded biphenyl and palladium metal,[2] presumably *via* a phenylpalladium complex obtained by electrophilic displacement of boron. Substitution of aromatic hydrogen by palladium salts to give similar intermediates was considered as a first step in coupling reactions of benzene and toluene.[2-4] The present work was undertaken in order to explore whether arylpalladium complexes could be prepared by desulfination of aromatic sulfinic acids. Sulfur dioxide eliminations of arenesulfinate complexes of transition metals have been reported,[5,6] and the preparation of arylmercuric chlorides from aromatic sulfinic acids and mercuric chloride (eq 1) has been known since 1905.[7]

$$\text{ArSO}_2\text{H} + \text{HgCl}_2 \xrightarrow[78°]{\text{H}_2\text{O-EtOH}} \text{ArHgCl} + \text{SO}_2 + \text{HCl} \quad (1)$$
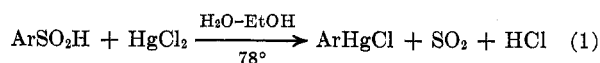
Attempts to replace HgCl₂ by thallic chloride in reaction 1 were unsuccessful.[8] Crystalline palladium arenesulfinate complexes have been prepared,[9,10] but their chemistry was not explored.

The present work shows that the addition of palladium salts to aromatic sulfinic acids in heated solution leads to evolution of sulfur dioxide, most likely by an electrophilic substitution process. The expected de-

composition products of the presumed arylpalladium intermediates, namely biaryls and palladium metal, were isolated. In Table I the experimental conditions and results of this new coupling reaction of sulfinic acids are summarized. The biaryls formed (biphenyl or *p,p'*-bitolyl) were identified by melting point, mixture melting point, ir, and glpc. Accordingly, the main reaction can be expressed as in eq 2. The yields

$$2\text{ArSO}_2\text{Na} + \text{Na}_2\text{PdCl}_4 \longrightarrow$$
$$\text{ArAr} + 2\text{SO}_2 + \text{Pd} + 4\text{NaCl} \quad (2)$$

of the by-products, aromatic hydrocarbon, arylchloride, and various sulfur products, depend strongly upon solvent and anion. Benzylacetate formed in entry 7 is a secondary product, derived from oxidation of toluene.

Mercuric chloride catalyzed the coupling reaction of aromatic sulfinic acids in aqueous solution, as reflected in the higher conversions to biaryls in Table II. The production of *p*-bromotoluene in entry 7, apparently derived by a ligand transfer reaction, prompted attempts to synthesize other *para*-substituted toluenes from *p*-toluenesulfinic acid, palladium chloride, and certain anions. However, experiments involving the anions X⁻ = F⁻, CN⁻, OCN⁻, N₃⁻, or NO₂⁻ did not yield any *p*-CH₃C₆H₄X. Entry 8 shows that a catalytic amount of palladium salt is sufficient in the presence of a reoxidizing agent like cupric chloride.

The intermediate formation of arylpalladium complexes in the desulfination of arenesulfinic acids with PdCl₂ was further substantiated by isolating the expected[1b] insertion products with carbon monoxide and olefins. The conversions in Table III again reflect strong solvent effects. Only the double insertion products (two *p*-tolyl groups per olefin) were formed with 1 atm of ethylene (entries 3 and 4). Occasionally the solvent added to the initial olefin or the olefinic product (entries 3, 5, and 8). The last two reactions represent additions of the *p*-tolylpalladium complex into CN triple bonds, a new type of insertion reaction of transition metal aryl complexes. The ketones isolated are

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