The formation of simple alkylchromium species is reminiscent of benzylchromium reported earlier[1a,9] and recently isolated as the pyridine complex.[10] The stabilities of these organochromium complexes are: benzyl > tertiary > secondary > primary. *t*-Butylchromium complex without its nitrogen-containing ligands can also be detected spectroscopically (4260 A) in the reaction between *t*-butyl iodide and chromous perchlorate in DMF. By analogy with benzylchromium, we postulate that these alkylchromium species are of the type $RCrL_n^{+2}$(L = en, ethanolamine, etc.).

Further studies on the use and identification of these chromium(II)–amine complexes as potent reducing agents, and characterization of the attendant chromium(III) species, are in progress.

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(9) F. A. L. Anet and E. LeBlanc, *J. Am. Chem. Soc.*, 79, 2649 (1957); J. K. Kochi and D. B. Buchanan, *ibid.*, **87**, 853 (1965).

(10) R. P. A. Sneeden and H. P. Throndsen, *Chem. Commun.*, 509 (1965); *cf.* R. G. Coombes, *et al.*, *ibid.*, 251 (1965); *J. Chem. Soc.*, 7029 (1965).

(11) We wish to thank the National Science Foundation for generous support of this research.

Jay K. Kochi, Paul E. Mocadlo[11]
Department of Chemistry, Case Institute of Technology
Cleveland, Ohio 44106

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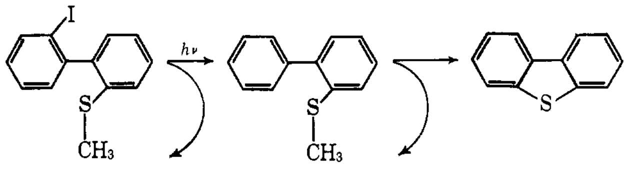
Radical Reactions of Organic Sulfides. II.[1] Behavior of the 2-(2′-Methylthio)biphenylyl Radical[2]

Sir:

The role of the sulfur atom in free-radical reactions of organic sulfides and disufides has been investigated previously because of the possible importance of octet expansion by sulfur. Various lines of evidence indicate that radicals are stabilized by an adjacent sulfur atom.[3] Bentrude and Martin[4] have presented striking kinetic evidence of anchimeric assistance by sulfides in homolytic perester decompositions. Radical displacements on the sulfur of disulfides have been recognized for some time[5] and have recently been studied in detail by Pryor and Guard.[6] We wish to report chemical evidence for the involvement of neighboring sulfur in the reactions of the 2-(2′-methylthio)biphenylyl radical (**2**). The general behavior of this radical constitutes the first example of a radical displacement[7] on the sulfur atom of a sulfide.

Photolysis of benzene solutions (10^{-3} to 10^{-2} *M*) of 2-iodo-2′-methylthiobiphenyl[8] (**1**) in a Vycor vessel with an external mercury resonance lamp[10] for 45–60 hr gives dibenzothiophene[11] in quantitative yields, toluene[11] (37–45%), and iodine (82%). Photolysis of **1** in a better hydrogen donor solvent, cyclohexane, is equally successful, giving dibenzothiophene in quantitative yield and iodine (65–70%). These observations are readily accommodated by a simple homolytic dissociation of the carbon–iodine bond of **1**, followed by rapid reaction of the carbon radical with the neighboring sulfide group.[12]



1 $I\cdot \rightarrow I_2$ **2** "$CH_3\cdot$" $\xrightarrow{C_6H_6} C_6H_5CH_3$

Several observations support the key role of the 2-(2′-methylthio)biphenylyl radical (**2**) in the ring closure to dibenzothiophene. Wolf and Kharasch[13] and others[14] have examined the photolyses of aryl iodides. These studies clearly indicate the formation of aryl radicals by dissociation of the carbon–iodine bond and therefore provide analogy for the production of radical **2**. More cogent is the fact that the 2-(2′-methylthio)biphenyl radical can be partially diverted by hydrogen transfer. Photolysis of **1** for 50 hr in *n*-butylthiol as solvent still gives dibenzothiophene as the major product (*ca.* 90%). Vapor phase chromatography of the reaction mixture, however, shows the product of hydrogen transfer to the radical, 2-thiomethylbiphenyl,[11] dibenzothiophene, and starting material in relative areas of 6:86:8.

Two further observations demonstrate that the formation of dibenzothiophene is a nonphotochemical, free-radical process. Reaction of **1** with 2 equiv of tri-*n*-butyltin hydride in refluxing toluene in the dark for 4.5 hr gives essentially quantitative conversion to dibenzothiophene. The rate of this reaction is markedly decreased by the presence of 7 mole % of a radical scavenger, trinitrobenzene. Since it is likely that the reaction of **1** with tri-*n*-butyltin hydride involves a radical chain mechanism,[15] radical **2** is implicated as a thermal precursor of dibenzothiophene. In addition 2-iodo-2′-methoxybiphenyl[16] was photolyzed in cyclohexane under conditions identical with those used for quantitative conversion of **1** to dibenzothiophene. Straightforward radical chemistry obtains, giving iodine (75%) and hydrogen transfer product, 2-methoxybiphenyl[11] (64%). The ratio of quantum yields for the initial production of iodine in cyclohexane from 2-iodo-2′-methoxybiphenyl and 2-iodo-2′-methylthiobiphenyl ($\phi_{I_2}^{OMe}/\phi_{I_2}^{SMe}$) is approximately 1.1. The similarity

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(1) Part I: J. A. Kampmeier, R. P. Geer, A. J. Meskin, and R. M. D'Silva, *J. Am. Chem. Soc.*, **88**, 1257 (1966).

(2) This work was supported by Public Health Service Research Grant CA-06535 from the National Cancer Institute.

(3) C. C. Price and J. Zomlefer, *J. Am. Chem. Soc.*, **72**, 14 (1950); C. E. Scott and C. C. Price, *ibid.*, **81**, 2672 (1959); R. F. Bridger and G. A. Russell, *ibid.*, **85**, 3754 (1963); G. Sosnovsky, *J. Org. Chem.*, **26**, 281 (1961).

(4) W. G. Bentrude and J. C. Martin, *ibid.*, **84**, 1561 (1962).

(5) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 332.

(6) W. A. Pryor and H. Guard, *J. Am. Chem. Soc.*, **86**, 1150 (1964).

(7) Displacement is used in a stoichiometric sense, without mechanistic implication.

(8) Compound **1**, mp 88.5–89.0°, is obtained in 49–64% yield by the thermal decomposition of dibenziodolium *t*-butyl mercaptide[9] in refluxing benzene containing a 20-fold excess of dimethyl disulfide. The corresponding sulfone, mp 150.5–152°, was prepared by the oxidation of **1** with hydrogen peroxide. Satisfactory analytical and spectral data were obtained for both compounds.

(9) J. W. Greidanus, W. J. Rebel, and R. B. Sandin, *J. Am. Chem. Soc.*, **84**, 1504 (1962).

(10) Hanovia SC 2537, Hanovia Chemical and Manufacturing Co., Newark, N. J.

(11) Most analyses were made by vpc. Materials were identified by both isolation and coinjection with authentic samples.

(12) The detailed nature of the methyl fragment and the route to toluene are not established by these experiments.

(13) W. Wolf and N. Kharasch, *J. Org. Chem.*, **30**, 2493 (1965).

(14) J. M. Blair, D. Bryce-Smith, and B. W. Pengilly, *J. Chem. Soc.*, 3174 (1959); J. M. Blair and D. Bryce-Smith, *ibid.*, 1788 (1960).

(15) L. W. Menapace and H. G. Kuivila, *J. Am. Chem. Soc.*, **86**, 3047 (1964); H. G. Kuivila, *Advan. Organometal. Chem.*, **1**, 47 (1964); D. H. Lorenz, P. Shapiro, A. Stern, and E. I. Becker, *J. Org. Chem.*, **28**, 2332 (1963).

(16) R. C. Fuson and R. L. Albright, *J. Am. Chem. Soc.*, **81**, 487 (1959).

of the quantum yields for the O-methyl and S-methyl compounds suggests that the photochemical processes are similar.[17] Product differences are determined in subsequent free-radical reactions.

In conclusion, these observations demonstrate an extremely rapid and efficient capture of an aryl radical by a neighboring sulfide group. The chemical consequence of this capture is an apparent displacement reaction at sulfur.

(17) This line of reasoning is not rigorous and would be incorrect if both compounds were photolyzed with quantum yields of unity. The S-methyl and O-methyl compounds, however, yield iodine with a quantum yield of *ca.* one-half that of ethyl iodide under comparable conditions. Although several values have been reported for the quantum yield for ethyl iodide in solution, the number is certainly less than one.[18] A quantum yield of 0.08 has been reported for the formation of iodine from 4-iodobiphenyl.[18]

(18) M. C. L. Gerry and G. B. Porter, *Nature*, **189**, 655 (1961).

J. A. Kampmeier, T. R. Evans
Department of Chemistry, University of Rochester
Rochester, New York 14627
Received July 5, 1966

Displacement Reactions on 2-Acetyl-3,4-dimethylthiazolium Iodide

Sir:

2-Acetyl-3,4-dimethylthiazolium iodide (I) serves as a model for 2-acetylthiamine, an intermediate in the phosphoketolase and α-keto oxidase reactions for which thiamine pyrophosphate is a cofactor.[1] Compound I has been prepared and noted to be unstable in aqueous or alcoholic solution[2] and to undergo reaction with water, hydroxylamine, and mercaptide ions to yield acetic acid, acethydroxamic acid, and thiolacetates, respectively.[3] Also, 2-benzoyl-3-methylthiazolium salts readily undergo solvolysis in methanol to give a 68% yield of methyl benzoate.[4] Aside from these few observations no one has carried out a general study of the susceptibility of I to nucleophilic attack nor have any kinetic studies of the displacement of the acyl group from I been reported. In the present communication we describe studies on the hydrolysis and hydroxylaminolysis of I; these studies provide an understanding of the nature of the acyl group of 2-acetylthiamine.

The hydrolysis of I was studied at 30° in water at an ionic strength of 1.0 (with KCl) by observing its conversion to 3,4-dimethylthiazolium ion at 292 mμ with the aid of a Gilford Model 2000 spectrophotometer or a stopped-flow spectrophotometer.[5] At each pH the observed pseudo-first-order rate constant (k_{obsd}, min^{-1}) was determined at ten buffer concentrations. Since the buffers did not influence the value of k_{obsd}, the value of the first-order solvolysis constant (k_1, min^{-1}) at each pH was taken as the average of the ten k_{obsd} constants. Buffers employed were: acetate (pH 4.07–5.18), succinate (pH 5.68), imidazole (pH 6.40–7.72), and Tris (pH 8.35–8.95). In Figure 1 are plotted the values of log k_1 *vs.* pH. It should be noted that the experimental points provide a precise fit to the theoretical line of slope 1.00 anticipated for a specific base catalyzed reaction and that the specific base rate law holds over 10^5 in hydrogen ion activity (a_H).

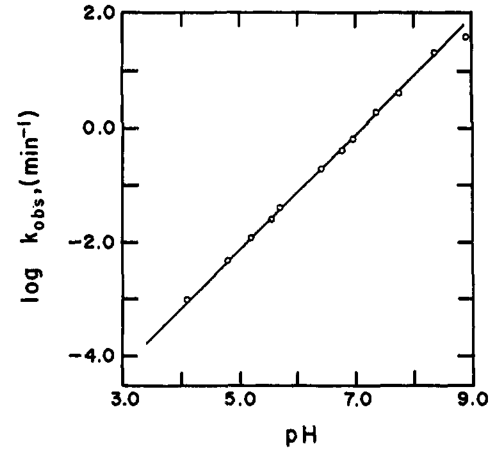
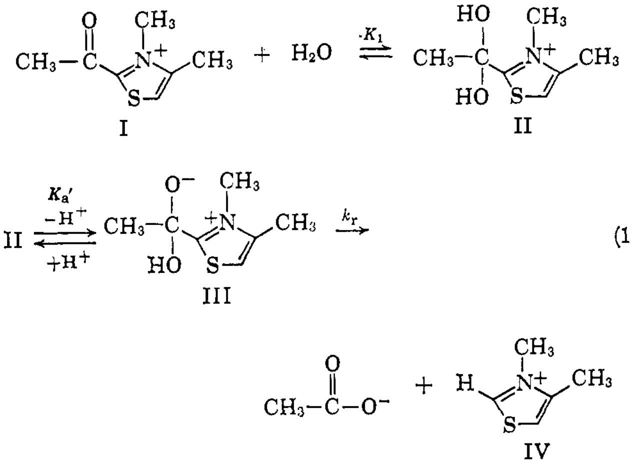


Figure 1.

From the knowledge that specific base catalysis predominates to pH 3 (and presumably to even lower pH values since the rate of hydrolysis of I is quite slow at pH values more acidic than 3) and that the nucleophilic species of the buffers employed do not enhance the rate of disappearance of I from solution, we conclude that the mechanism of hydrolysis of I is that shown in Scheme I. For Scheme I in the pH range below pK_a'

Scheme I



(1)

$$\frac{-d[I]}{dt} = \left[\frac{k_rK_1K_a'}{K_w(K_1 + 1)}\right][OH^-]([I] + [II]) \qquad (2)$$

where K_w is the autoprotolysis constant for water at 30°. Comparison of (2) to the experimental rate law (3) establishes the second-order rate constant for alkaline

$$\frac{-d[I]}{dt} = k_{OH}[OH^-]([I] + [II]) \qquad (3)$$

hydrolysis (k_{OH}) to be

$$k_{OH} = \frac{k_rK_1K_a'}{K_w(K_1 + 1)} = 5.64 \times 10^{+6}\ \text{l. mole}^{-1}\ \text{min}^{-1} \qquad (4)$$

That k_{OH} could not represent the second-order rate constant for direct nucleophilic attack of $[OH^-]$ on the

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(1) For a review of the literature see: T. C. Bruice and S. J. Benkovic, "Bioorganic Mechanisms," Vol. II, W. A. Benjamin, Inc., New York, N. Y., 1966, Chapter 8.

(2) R. Breslow and E. McNelis, *J. Am. Chem. Soc.*, **82**, 2394 (1960).

(3) K. Daigo and L. J. Reed, *ibid.*, **84**, 659 (1962).

(4) F. G. White and L. L. Ingraham, *ibid.*, **82**, 4114 (1960); **84**, 3109 1962).

(5) T. C. French, S. J. Benkovic, and T. C. Bruice, *Rev. Sci. Instr.*, **36**, 860 (1965).