(9) A more complete discussion of this reaction will be given in a later paper in this series.
(10) These salts as hydrates are difficult to analyze and their assignment is based on their spectral properties and comparison with model systems such as **2**.
(11) The KBr IR spectrum of perchlorate **1a** was performed before its explosive nature was appreciated.
(12) In fluorosulfonic acid this singlet remained almost invarient over a temperature range of −60 to +60 °C. No change was observed for **1a** in the ^{13}C NMR chemical shift difference ($\Delta^{N\text{-}Me}$ = 30 Hz) when the temperature was raised from 30 to 80 °C.
(13) A method for synthesizing mixed iminium salts (e.g., **1d**) will be described in a later paper.
(14) Characterization of **6** is based on the similarity of its spectral properties with **1c**. ^1H NMR (δ, CD_3CN): **6**, 1.78 (3 H, br s), 4.00 (2 H, br s); **1c**, 1.76 (3 H, br s), 4.03 (2 H, br s). The UV spectrum in 70% $HClO_4$ displays the expected bathochromic shift in going from **1c** to **6** (λ_{1c} 255 nm, λ_6 275 nm).
(15) See following paper in this issue by R. R. Schumaker and E. M. Engler.

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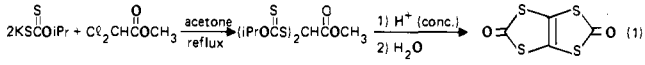
Thiapen Chemistry. 2. Synthesis of 1,3,4,6-Tetrathiapentalene-2,5-dione

Sir:

In the preceding communication,[1] a new heterocyclic ring system, 1,3,4,6-tetrathiapentalene (abbreviated thiapen) was prepared as a 2,5-bis(dialkyliminium) salt by reacting a dialkylcarbamate with methyl dichloroacetate, followed by cyclization in acid. Attempts to convert the iminium groups to functional groups suitable for the elaboration of tetrathiafulvalene derivatives[2] were unsuccessful. This problem has been circumvented by employing an *O*-alkyldithiocarbonate in place of the carbamate. This permits the preparation of 1,3,4,6-tetrathiapentalene-2,5-dione (**1**, abbreviated thiapendione), analogous with previous work on the preparation of 1,3-dithiole-2-ones.[3]

Reaction of methyl dichloroacetate with 2 mol equiv of potassium *O*-isopropyldithiocarbonate in refluxing acetone provided in quantitative yield methyl 2,2-bis(*O*-isopropyldithiocarbonyl)acetate (**2**)[4] as a light yellow oil. This material



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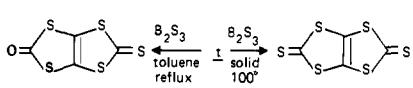
could be readily cyclized to the thiapen ring system[5] with concentrated H_2SO_4 at 0–5 °C and isolated as the 2,5-dione derivative (**1**) on addition to ice–water (eq 1). Crystallization from acetonitrile gives thiapendione **1** as long white needles in 70–80% yield (mp 150 °C; IR (KBr, cm^{-1}) 1727 (m), 1678 (s), 973 (w); 914 (w); UV (λ_{max}, nm, methanol) 273, 222; mol wt calcd 207.878, found (mass spectroscopy) 207.878). Thiapendione is a central precursor for the preparation of a wide variety of novel organosulfur compounds. Some illustrative examples follow.

Depending on reaction condition, thiapendione can be converted on treatment with boron sulfide into either the mixed carbonyl–thiocarbonyl derivative **3** or the dithiocarbonyl derivative **4**. Thus, treatment of **1** with boron sulfide in refluxing



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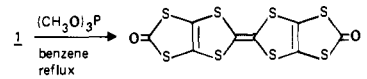
toluene afforded **3** (mp 176–179 °C dec; IR (KBr, cm^{-1}) 1727 (w), 1700 (m), 1675 (m), 1083 (s), 968 (w), 900 (w); mol wt calcd 223.855, found (mass spectroscopy) 223.853) as the major product with minor amounts of **1** and **4** also present. These impurities could be separated by chromatography. When a solid mixture of **1** and boron sulfide is heated overnight at 100 °C, dithione **4** is obtained as a yellow solid (mp 207–210 °C dec; IR (KBr, cm^{-1}) 1068 (s), 959 (m), 900 (w), 776 (w); mol wt calcd 239.832, found (mass spectroscopy) 239.831).

Treatment of **1** with trimethyl phosphite in refluxing benzene precipitated the dimerized system **5** (dithiapendione)[4] as a very insoluble olive powder in 75% yield (mp >360 °C; IR



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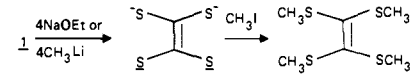
(KBr, cm^{-1}) 1740 (m), 1720 (s), 1700 (s), 1510 (w), 970 (w), 880 (w), 845 (w), 765 (w), 745 (m)). No higher coupled homologues (trimers, etc.) were detected, even under more strenuous reaction conditions.

Reaction of **1** or **5** under nitrogen with 4 mol equiv of sodium ethoxide in refluxing ethanol or methyllithium in tetrahydrofuran at room temperature afforded the corresponding air-sensitive tetrathiolate salts[6] **6** and **7** which could be con-



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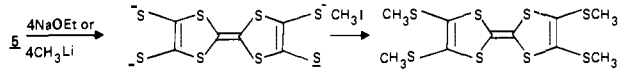
verted on addition of methyl iodide to the *known* compounds: tetrathiomethoxyethylene (**8**)[7] and tetrathiomethoxytetrathiafulvalene (**9**),[8] respectively.[9] TTF derivative **9** reacts with TCNQ in nitroethane at low temperature to give a blue-black 1:0.9 charge-transfer salt with a room temperature compaction conductivity of $2.5 \times 10^{-4}\,\Omega$ cm.



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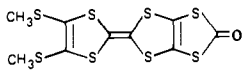
When only 2 mol equiv of sodium ethoxide or methyllithium are added to **5** and subsequently treated with methyl iodide, the half-opened dithiomethoxy derivative (**10**)[10] can be isolated



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in low yield after chromatography (mp 178 °C dec; IR (KBr, cm^{-1}) 2900 (m), 1660 (s), 1610 (m), 1420 (m), 965 (w), 875 (m), 765 (w) 750 (m); NMR (δ, $CDCl_3$) 2.40).[11]

While dimer **5**, a tetrathiafulvalene derivative, appears to be unreactive with TCNQ, monomer **1**, surprisingly, forms a 1:1 blue-black charge-transfer salt with TCNQ[4] with a room temperature compaction conductivity of $10^{-8}/\Omega$ cm.

Further elaboration of the chemistry of thiapendione, including capping reactions with 1,3-dithiole derivatives,[12] will be reported shortly.

Acknowledgments. We thank A. A. Fukushima and V. V. Patel for their experimental assistance and R. Greene for carrying out the conductivity measurements.

References and Notes

(1) R. R. Schumaker and E. M. Engler, *J. Am. Chem. Soc.*, preceding paper in this issue.
(2) A number of tetrathiafulvalene derivatives react with acceptors to form the most conducting organic solids presently known. Reviews: M. Narita and C. U. Pittman, Jr., *Synthesis*, 489 (1976); E. M. Engler, *Chem. Technol.*, **6**, 274 (1976).
(3) E. Campaigne, R. D. Hamilton, and N. W. Jacobsen, *J. Org. Chem.*, **29**, 1708 (1964); I. D. Rae, *Int. J. Sulfur Chem.*, **1**, 59 (1971); A. K. Bhattacharya and

A. G. Hortmann, *J. Org. Chem.*, **39**, 95 (1974), and references cited therein.
(4) All new materials gave satisfactory spectral data consistant with the assigned structures. Elemental analyses were within acceptable limits for **1**, **2**, **4**, **5**, and the TCNQ salts of **1** and **9**. Compound **3** contained a trace of **1** (mass spectroscopy and analysis) which was retained after repeated chromatography. No analysis of **10** was carried out owing to insufficient material; however see ref 11.
(5) Attempts to carry out the sequence of reactions described in eq 1 with potassium *O*-isopropyldiselenocarbonate have so far been unsuccessful.
(6) The reaction of tetrathiolate salts, **6** and **7**, with transition metal salts to give the corresponding metal dithiolene derivatives will be described in a subsequent paper: R. R. Schumaker, e. M. Engler, and N. Martinez, unpublished work. Solt **6** has previously been prepared by another route (F. Wudl, private communication).
(7) U. Schöllkopf and E. Wiskott, *Angew. Chem., Int. Ed. Engl.*, **2**, 485 (1963); D. M. Lemal and E. H. Banitt, *Tetrahedron Lett.*, 245 (1964).
(8) P. R. Moses and J. Q. Chambers, *J. Am. Chem. Soc.*, **96**, 945 (1974).
(9) Previously, this type of reaction has been carried on the 1,3-dithiole ring system with a carbonyl group (R. Mayer and B. Gebhardt, *Ber.*, **97**, 1298 (1964)) and with a thiocarbonyl group (M. Mizuno, M. P. Cava, and A. F. Garito, *J. Org. Chem.*, **41**, 1484 (1976)).
(10) Thiapen-2-one-5-(dithiomethoxy-1′,3′-dithioliden-2′-yl).
(11) Mass spectrum peak match gave 385.819; calcd for $C_9H_6S_8O$ 385.818.
(12) R. R. Schumaker and E. M. Engler, unpublished work.

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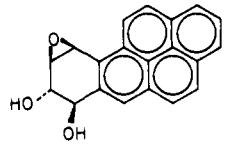
Changes of Mechanisms and Product Distributions in the Hydrolysis of Benzo[*a*]pyrene-7,8-diol 9,10-Epoxide Metabolites Induced by Changes in pH

Sir:

Numerous investigations from several laboratories have indicated that diol epoxides **1** and **2**[1] play a dominant role in



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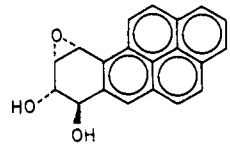

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the cytotoxic, mutagenic,[2] and carcinogenic[3] action of the ubiquitous environmental carcinogen benzo[*a*]pyrene. Thus, a knowledge of the solvolytic reactions of these metabolites[4] assumes a special importance. To date, only product studies with qualitative rate data,[2a,4b,5] and one kinetic study[6] over a very limited pH range (ca. 5-6) in 50% dioxane-water have appeared. In the latter study, kinetic data revealed only the existence of acid-catalyzed mechanisms for the hydrolysis of **1** and **2**, and both isomers were found to possess similar reactivities.[7] The present study reports the pH-rate profiles and product analysis for the hydrolysis of **1** and **2** in water and in dioxane-water mixtures. *This study reveals that the mechanisms for hydrolysis of both* **1** *and* **2** *change from acid-catalyzed processes at low pH to spontaneous reactions with solvent at higher pH in highly aqueous solutions (Figure 1), accompanied by changes in product distributions.* Whereas isomer **2** is about twice as reactive as isomer **1** toward acid-catalyzed hydrolysis, **1** is more than 30 times more reactive than **2** under conditions of spontaneous hydrolysis. The large difference in reactivity between **1** and **2** in the physiological pH range may play a significant role in the relative tumorgenic properties of **1** and **2**.

The pH-rate profiles for the hydrolysis of **1** and **2** in water and in 25% dioxane-water are given in Figures 1 and 2.[8] The plots of log k_{obsd} vs. pH for **1** and **2** in water exhibited slopes of −1 at low pH, which indicated the predominance of acid-catalyzed mechanisms for hydrolysis. However, at pH > ca. 5 for **1** and 7 for **2**, the profiles leveled out until finally the rates of hydrolysis were independent of pH. These data demonstrate

Table I. Rate Constants for Hydrolysis of **1** and **2** in Water and Dioxane-Water Mixtures at 25 °C[a,b]

Compound	Solvent	k_{H+}, M^{-1} s^{-1}	k_0, s^{-1}
1	Water	$5.8 \pm 0.9 \times 10^2$	$1.8 \pm 0.1 \times 10^{-2}$
2		$1.4 \pm 0.2 \times 10^3$	$5.4 \pm 0.8 \times 10^{-4}$
1	10% dioxane-water[c]	$5.1 \pm 0.4 \times 10^2$	$4.2 \pm 0.3 \times 10^{-3}$
2		$1.4 \pm 0.2 \times 10^3$	$1.3 \pm 0.5 \times 10^{-4}$
1	25% dioxane-water[c]	$4.1 \pm 0.1 \times 10^2$	$7.2 \pm 0.3 \times 10^{-4}$
2		$7.9 \pm 0.2 \times 10^2$	

[a] Ionic strength = 0.1 ($NaClO_4$). Rate constants were calculated from weighted least-squares plots of k_{obsd} vs. a_{H+}. All solutions contained 10^{-4} M ethylenediaminetetraacetic acid (EDTA). Rates were monitored by observing the absorbance change of the reaction solution at 278-279 nm in the thermostated cell compartment (25.0 ± 0.2 °C) of a Gilford 2400 spectrophotometer. [b] Reference 8. [c] v/v.

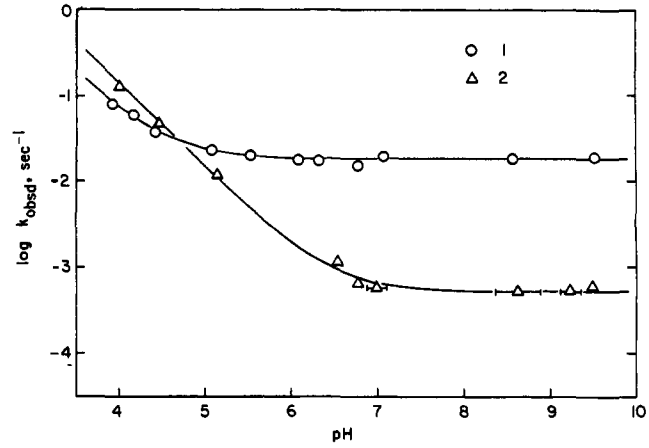

Figure 1. Plots of log k_{obsd} vs. pH for hydrolysis of **1** and **2** in water (0.1 M $NaClO_4$, 10^{-4} M EDTA), 25 °C. The pH range throughout any given run was generally <0.05 pH unit. Several kinetic solutions for **2** underwent a greater pH change in the plateau region, and the ranges are represented by horizontal error bars.

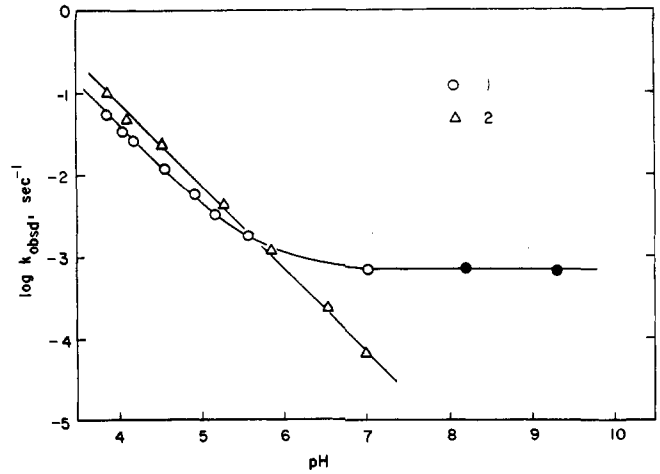

Figure 2. Plots of log k_{obsd} vs. pH for hydrolysis of **1** and **2** in 25% dioxane-water (0.1 M $NaClO_4$, 10^{-4} M EDTA), 25 °C. Several kinetic solutions (●) for **1** contained Tris buffer (total buffer concentration 0.02 M).