Registry No.—**1**α, 13096-56-5; **1**β, 13096-57-6; **2**α, 10396-60-1; **2**β, 13096-61-2; **3**, 16354-75-9; **4**, 16354-76-0; **5**α, 16354-77-1; **5**β, 16354-78-2; **6**α, 16354-79-3; **6**β, 16354-80-6; **7**α, 16354-81-7; **7**β, 16354-82-8; **8**α, 16354-83-9; **8**β, 16354-84-0; **9**, 3353-98-8; **10**, 16354-86-2.

Reactions of Mercuric Salts with Bis(diethylthiocarbamoyl) Disulfide and Benzenesulfenyl Chloride

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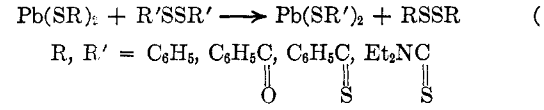
When mercuric carboxylates were treated with bis(diethylthiocarbamoyl) disulfide (**1**), acid anhydrides were obtained in good yields along with mercuric diethyldithiocarbamate and an unidentified oxygenated product. Further, it was found that treatment of mercuric carboxylates with 2 equiv of benzenesulfenyl chloride (**5**) gave acid anhydrides, diphenyl disulfide, and mercuric chloride in high yields. A transient intermediate of this reaction, sulfenyl carboxylate, was trapped by treating a mercuric carboxylate with **5** in the presence of an olefin. Reactions of mercuric thiolates with these organic sulfur compounds were also studied.

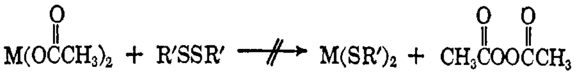
As part of a continuing study on the behavior of organic sulfur compounds in redox reaction systems, reactions of lead thiolates with disulfides were examined in our laboratory[1] (eq 1). It was concluded that the



$$\mathrm{Pb(SR)_2 + R'SSR' \longrightarrow Pb(SR')_2 + RSSR} \qquad (1)$$
$$\mathrm{R,\ R' = C_6H_5,\ C_6H_5\underset{O}{\underset{\|}{C}},\ C_6H_5\underset{S}{\underset{\|}{C}},\ Et_2N\underset{S}{\underset{\|}{C}}}$$

oxidizing power of the disulfides increases in the following order: diphenyl disulfide < dibenzoyl disulfide < bis(thiobenzoyl) disulfide < bis(diethylthiocarbamoyl) disulfide. The present paper deals with the reactions of some mercuric salts, such as mercuric carboxylates and mercuric thiolates, with some sulfides or benzenesulfenyl chloride.

In the first place, the reaction of a metal salt having the metal–oxygen bond, such as lead, silver, zinc, and mercuric acetates, was tried with the assumption that an oxidative coupling product, organic diacyl peroxide, and a metal salt of a thiol would result by the following redox reaction (eq 2). Among various metal acetates



$$\mathrm{M(O\overset{O}{\overset{\|}{C}}CH_3)_2 + R'SSR' \not\longrightarrow M(SR')_2 + CH_3\overset{O}{\overset{\|}{C}}OO\overset{O}{\overset{\|}{C}}CH_3} \qquad (2)$$

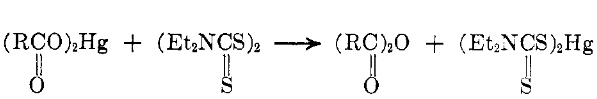
examined, mercuric and silver[2] acetates were found to react with bis(diethylthiocarbamoyl) disulfide (**1**) at room temperature, while cadmium, lead, and zinc acetates did not react in boiling chloroform. In addition, it was established that diphenyl disulfide and dibenzoyl disulfide did not react with mercuric acetate in boiling chloroform, and the starting materials were recovered quantitatively. This result suggests that the reactivities of the disulfides in this reaction depend on the oxidizing power of the disulfides.

Next, the reactions of various mercuric carboxylates with disulfide **1** were studied in detail. Contrary to our expectations, diacyl peroxides could not be obtained when mercuric carboxylates were treated with **1** at room temperature. Instead, acid anhydrides and mercuric diethyldithiocarbamate (**2**) were obtained in good yields together with a substantial amount of a yellow precipitate. Similarly, the anhydride of carbobenzyloxyglycine was also obtained from the corresponding mercuric salt in 72% yield as shown in Table I. However, when mercuric propionate or benzoate was allowed to react with **1** in the presence of water under the same conditions, 66 or 95% of the corresponding acid and 86 or 96% of **2** were obtained. Gas evolution was not observed in the reaction (eq 3).

Table I

Reactions of Mercuric Carboxylates with Bis(diethylthiocarbamoyl) Disulfide

Mercuric carboxylate	Solvent	Yield, %	
		Anhydride	$\mathrm{(Et_2N\underset{S}{\underset{\|}{C}}S)_2Hg}$
Acetate	Benzene	68	75
Propionate	CH_2Cl_2	84	50
Butyrate	CH_2Cl_2	86	54
Benzoate	CH_2Cl_2	67	53
Succinate	CH_2Cl_2	88	76
Phthalate	Benzene	57	76
Cbo-Gly	Dioxane	72	68



$$\mathrm{(R\underset{O}{\underset{\|}{C}}O)_2Hg + (Et_2N\underset{S}{\underset{\|}{C}}S)_2 \longrightarrow (R\underset{O}{\underset{\|}{C}})_2O + (Et_2N\underset{S}{\underset{\|}{C}}S)_2Hg} \qquad (3)$$

1 **2**

The structure of **2** was confirmed by elemental analysis and the infrared spectrum. In the case of mercuric acetate, propionate, and butyrate, the yellow precipitate decomposed in the reaction mixture at room temperature in about 20 min into a black solid. This may be mercuric sulfide. With mercuric succinate and phthalate, the yellow precipitate (**3**) was rather stable and could be isolated. Compound **3** might be an oxygenated product. The infrared spectrum of **3** showed a strong band at 1700 cm^{-1}. Recrystallization of **3** from acetonitrile gave pale yellow crystals (**4**) whose infrared spectrum differed from that of **3**. The infrared spectrum of **4** was almost identical with that of **2**, but showed no band at 1700 cm^{-1}. Elemental analysis and the infrared spectrum of **4** indicated a molecular formula of $C_{10}H_{20}N_2O_6S_4Hg$ or $C_{10}H_{20}N_2O_4S_5Hg$, which corresponds formally to a combination of **2** and O_6 or of **2**, SO_2, and O_2, but its structure

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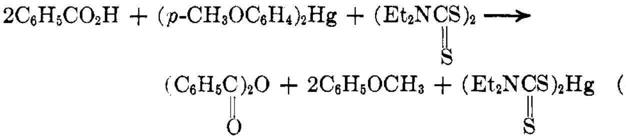
[1] T. Mukaiyama and T. Endo, *Bull. Chem. Soc. Jap.*, **40**, 2388 (1967).

[2] In this case, only silver diethyldithiocarbamate could be isolated in 94% yield.

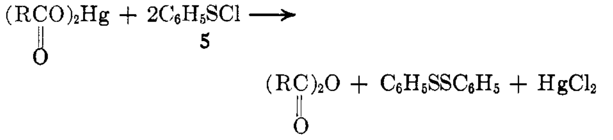
remains unknown. As demonstrated above, the mechanism for this reaction has not yet been established.

Further, an anhydride was prepared by a one-step procedure[3] from a free carboxylic acid, diarylmercury, and **1**. When 2 equiv of benzoic acid and di-*p*-anisylmercury were allowed to react with **1** in boiling benzene for 30 min, benzoic anhydride (72%) and **2** (50%) were obtained along with a substantial amount of a black solid (eq 4).



$$2\mathrm{C_6H_5CO_2H} + (p\text{-}\mathrm{CH_3OC_6H_4})_2\mathrm{Hg} + (\mathrm{Et_2N}\underset{\underset{\displaystyle \mathrm{S}}{\|}}{\mathrm{C}}\mathrm{S})_2 \longrightarrow (\mathrm{C_6H_5}\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}})_2\mathrm{O} + 2\mathrm{C_6H_5OCH_3} + (\mathrm{Et_2N}\underset{\underset{\displaystyle \mathrm{S}}{\|}}{\mathrm{C}}\mathrm{S})_2\mathrm{Hg} \quad (4)$$

It was also expected that the use of sulfenyl chloride in place of disulfide **1** in the above reaction (eq 3) would lead to the formation of acid anhydrides along with the disulfide and mercuric chloride. Indeed, mercuric carboxylates reacted readily with 2 equiv of benzenesulfenyl chloride (**5**) at room temperature to give acid anhydrides, diphenyl disulfide, and mercuric chloride in high yields.[4] However, when methyl benzenesulfenate or N,N-diethylbenzenesulfenamide was used as the sulfenyl compound in this reaction, no reaction occurred, and the starting materials were recovered almost quantitatively. No gas evolution was observed in the reaction with benzenesulfenyl chloride (eq 5). The anhydrides were obtained by a simple procedure. After separating mercuric chloride and acid anhydrides, diphenyl disulfide was isolated by chromatography over alumina using ether as an eluent. During this procedure an oxygenated product containing an organic sulfur compound might be adsorbed in alumina as an ether-soluble mercury complex. It should be noted that the yields of diphenyl disulfide were always less than 75% as shown in Table II. It is interesting to note that sulfenyl chloride **5** and disulfide **1** behaved similarly toward mercuric carboxylates to give acid anhydrides in high yields.



$$(\mathrm{R}\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{O})_2\mathrm{Hg} + \underset{\mathbf{5}}{2\mathrm{C_6H_5SCl}} \longrightarrow (\mathrm{R}\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}})_2\mathrm{O} + \mathrm{C_6H_5SSC_6H_5} + \mathrm{HgCl_2} \quad (5)$$

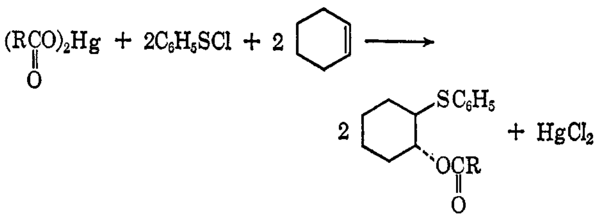
TABLE II

REACTIONS OF MERCURIC CARBOXYLATES WITH BENZENESULFENYL CHLORIDE

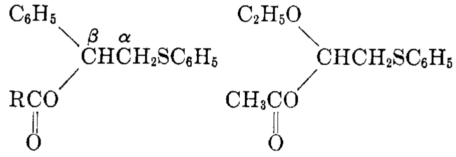
Mercuric carboxylate	Solvent	Yield, %: Anhydride	Yield, %: C_6H_5SS-C_6H_5	Yield, %: $HgCl_2$
Acetate	Ether	69	75	80
Propionate	Ether	61	71	82
Butyrate	Ether	85	74	83
Benzoate	CH_2Cl_2	80[a]	66	92
Succinate	CH_2Cl_2	91	75	92
Phthalate	CH_2Cl_2	81	72	90

[a] Since benzoic anhydride could not be separated from diphenyl disulfide by fractional distillation, the yield was determined from the weight of the corresponding anilide derived from the anhydride.

Furthermore, in connection with investigations of the mechanism of the reaction (eq 5), some attempts to trap a transient intermediate were made. When a mercuric carboxylate was allowed to react with 2 equiv of **5** in the presence of 2 equiv of cyclohexene at room temperature in methylene chloride, the addition product, 2-acyloxycyclohexyl phenyl sulfide (**6**), and mercuric chloride were obtained in good yields (eq 6). The acid anhydride and diphenyl disulfide could not be isolated. The formation of **6** would be explained by assuming that phenylthio and acyloxy moieties or benzenesulfenyl carboxylates[5] initially formed from mercuric carboxylates and **5** might add faster to cyclohexene than sulfenyl chloride[6,7] (**5**). Similar adducts (**7** and **8**) were obtained when styrene or ethyl vinyl ether was used as an "acceptor" in the above reaction (eq 6). Physical properties and analytical data of these adducts are listed in Table III. On the other hand, no addition product was formed with acrylonitrile and chalcone under the same conditions. The observed olefinic reactivity would be explained by the familiar argument.


(6)

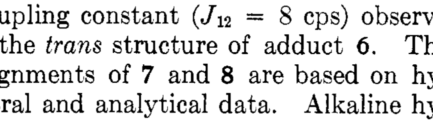
6a, R = CH_3
b, R = C_6H_5



7a, R = CH_3
b, R = C_6H_5

8

The coupling constant (J_{12} = 8 cps) observed for **6** supports the *trans* structure of adduct **6**. The structural assignments of **7** and **8** are based on hydrolysis and spectral and analytical data. Alkaline hydrolysis of **7b** gave the corresponding alcohol[8] (**9**) and benzoic acid in 70 and 82% yields, respectively. The methylene protons of **7** resonated as two quartets with a geminal coupling constant of 14 cps and vicinal J of 6 and 8 cps. This pattern is explained by nonequivalency of the methylene protons. The quartet at



$$\mathbf{7b} \xrightarrow{\mathrm{OH^-}} \underset{\mathbf{9}}{\mathrm{C_6H_5}\underset{\underset{\displaystyle \mathrm{OH}}{|}}{\mathrm{C}}\mathrm{HCH_2SC_6H_5}} + \mathrm{C_6H_5CO_2H} \quad (7)$$

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[3] T. Mukaiyama, I. Kuwajima, and Z. Suzuki, *J. Org. Chem.*, **28**, 2024 (1963).

[4] Further reactions of **5** were tried by the use of the other metal carboxylates. In the case of silver acetate or benzoate, 69 or 71% of the corresponding anhydride, 72 or 68% of diphenyl disulfide, and 95 or 92% of silver chloride were obtained, respectively. With cupric benzoate, a black precipitate was formed, which, on filtration, rapidly decomposed to a pale blue solid presumably by moisture.

[5] (a) A. J. Havlik and N. Kharasch, *J. Amer. Chem. Soc.*, **78**, 1207 (1956); (b) R. E. Putnam and W. H. Sharkey, *ibid.*, **79**, 6526 (1957).

[6] G. Wittig and F. Vidal, *Chem. Ber.*, **81**, 368 (1948).

[7] (a) N. Kharasch and C. M. Buess, *J. Amer. Chem. Soc.*, **71**, 2724 (1949); (b) D. J. Cram, *ibid.*, **71**, 3884 (1949); (c) S. J. Cristol, R. P. Arganbright, G. D. Brindell, and R. M. Heitz, *ibid.*, **79**, 6035 (1957).

[8] R. F. Brookes, J. E. Cranham, D. Greenwood, and H. A. Stevenson, *J. Sci. Food Agr.*, **8**, 561 (1957).

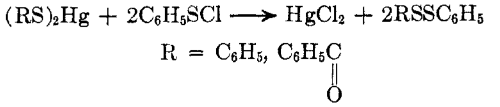
TABLE III

PHYSICAL PROPERTIES AND ANALYTICAL DATA FOR THE ADDUCTS

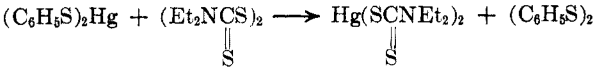
Compd	R	Yield, %	Bp (mm), °C	$n^{25}D$	Formula	Calcd, % C	Calcd, % H	Found, % C	Found, % H
6a	CH_3	80	119–120 (0.08)	1.5890	$C_{14}H_{18}O_2S$	67.18	7.25	66.89	6.99
6b	C_6H_5	59	168–169 (0.08)	1.5960	$C_{19}H_{20}O_2S$	73.06	6.45	72.89	6.73
7a	CH_3	77	131–132 (0.03)	1.5819	$C_{16}H_{16}O_2S$	70.57	5.92	70.39	6.21
7b	C_6H_5	66	189–190 (0.08)	1.6248	$C_{21}H_{18}O_2S$	75.43	5.43	75.15	5.39
8		59	100–101 (0.09)		$C_{12}H_{16}O_3S$	59.99	6.71	60.14	6.74

τ 3.93 assigned to the $C_\beta H$ proton of **7b** was shifted high field 1.55 ppm in **9**, indicating that the benzoyloxy group of **7b** is attached to the β carbon.

Finally, reactions of mercuric thiolates were investigated. Treatment of mercuric benzenethiolate or thiobenzoate with 2 equiv of **5** at room temperature afforded 89 or 82% of mercuric chloride and 97% of diphenyl disulfide or 80% of benzoyl phenyl disulfide, respectively. In addition, it was found that mercuric benzenethiolate reacted readily with **1** at room temperature to give **2** (95%) and diphenyl disulfide (98%), as expected.



$$(RS)_2Hg + 2C_6H_5SCl \longrightarrow HgCl_2 + 2RSSC_6H_5 \qquad (8)$$
$$R = C_6H_5,\ C_6H_5\underset{\underset{O}{\|}}{C}$$



$$(C_6H_5S)_2Hg + (Et_2N\underset{\underset{S}{\|}}{C}S)_2 \longrightarrow Hg(S\underset{\underset{S}{\|}}{C}NEt_2)_2 + (C_6H_5S)_2 \qquad (9)$$

In conclusion, it is of special interest to note that there are essential differences in behavior between mercuric compounds containing the Hg–O bond and those containing the Hg–S bond toward sulfenyl chloride **5** or disulfide **1**.

Experimental Section[9]

Materials.—Cadmium, lead, mercuric, silver, and zinc acetates were commercial materials and used without further purification. The other mercuric carboxylates,[10] cupric benzoate,[11] silver benzoate,[12] and mercuric benzenethiolate[13] were prepared as previously described. Diphenyl disulfide, dibenzoyl disulfide, bis(diethylthiocarbamoyl) disulfide (**1**), benzenesulfenyl chloride (**5**), and the related sulfenyl compounds were prepared in the usual manner.

Preparation of Mercuric Thiobenzoate.—This compound was prepared from mercuric acetate and 2 equiv of thiobenzoic acid[14] in methylene chloride and recrystallized from ethanol to give white needles: mp 140–141°; ν_{max}^{KBr} 1625, 1610, 1200, and 900 cm^{-1}.

Anal. Calcd for $C_{14}H_{10}O_2S_2Hg$: C, 35.41; H, 2.12. Found: C, 35.14; H, 2.08.

Reaction of Mercuric Acetate and Disulfide 1.—Mercuric acetate (6.38 g, 0.02 mol) was added to a solution of **1** (5.95 g, 0.02 mol) in 40 ml of benzene with stirring at room temperature over a period of 5 min. An exothermic reaction took place immediately and a pale yellow precipitate was formed. This decomposed to a fine black solid in about 20 min at room temperature. The black reaction mixture was concentrated, cooled at 0°, and treated with ether. The black crystalline material was collected by filtration and extracted with methylene chloride. The filtrate was distilled to give acetic anhydride (1.34 g, 68%), bp 51–52° (25 mm), $n^{25}D$ 1.3898, whose infrared spectrum was identical with that of an authentic sample. The residue was extracted with methylene chloride. The combined extracts were evaporated *in vacuo* to give **2** (7.51 g, 75%), mp 132–134°. Recrystallization from acetonitrile gave an analytically pure yellow crystal: mp 138–139°; ν_{max}^{KBr} 1495, 1425, 1270, and 1200 cm^{-1}.

Anal. Calcd for $C_{10}H_{20}N_2S_4Hg$: C, 24.17; H, 4.05; N, 5.64. Found: C, 24.33; H, 3.92; N, 5.81.

By a similar procedure, propionic, butyric, and benzoic anhydrides were obtained (see Table I).

Reaction of Mercuric Phthalate with 1.—To a stirred solution of **1** (2.96 g, 0.01 mol) in 30 ml of benzene was added mercuric phthalate (3.65 g, 0.01 mol) at room temperature. After stirring was continued for 10 min, 1.45 g of a pale yellow precipitate (**3**) was collected by filtration. The infrared spectrum showed bands at 1700, 1510, 1430, and 1280 cm^{-1}. Except for acetonitrile, DMF, DMSO, and pyridine, compound **3** was insoluble in most organic solvents. Recrystallization from acetonitrile gave analytically pure yellow crystals (**4**): mp 159–160°; ν_{max}^{KBr} 1495, 1420, 1275, and 1200 cm^{-1}.

Anal. Calcd for $C_{10}H_{20}N_2O_6S_4Hg$ or $C_{10}H_{20}N_2O_4S_5Hg$: C, 20.25; H, 3.39; N, 4.72. Found: C, 20.06; H, 3.22; N, 4.73.

The filtrate was concentrated and treated with ethanol. The resulting crystals of **2** (3.80 g, 76%), mp 133–135°, were filtered. Evaporation of ethanol from the filtrate gave phthalic anhydride (0.85 g, 57%), mp 127–128°, whose infrared spectrum was identical with that of an authentic sample. The mixture melting point with an authentic sample showed no depression.

By a similar procedure, anhydrides of carbobenzyloxyglycine and succinic acid were obtained (see Table I).

Reaction of Mercuric Benzoate with 1 in the Presence of Water.—To a stirred mixture of mercuric benzoate (4.45 g, 0.01 mol) and water (0.4 g, 0.02 mol) in 30 ml of methylene chloride was added **1** (2.96 g, 0.01 mol) at room temperature. A slightly exothermic reaction was observed. After stirring was continued for 10 min, a small amount of a pale yellow precipitate was removed by filtration. The filtrate was concentrated and treated with ether. The yellow crystals of **2** (4.81 g, 96%), mp 135–137°, were collected by filtration. Evaporation of ether from the filtrate gave benzoic acid (2.32 g, 95%), mp 112–115°, whose infrared spectrum was identical with that of an authentic sample.

Similarly, propionic acid (66%) and **2** (86%) were obtained by the reaction of mercuric propionate with **1** in the presence of water.

Reaction of Di-*p*-anisylmercury and Benzoic Acid with 1.—A mixture of di-*p*-anisylmercury (4.15 g, 0.01 mol) and benzoic acid (2.45 g, 0.02 mol) in 20 ml of benzene was refluxed for 20 min. To this was added a solution of **1** (2.96 g, 0.01 mol) in 10 ml of benzene, and the mixture was refluxed for 30 min. A black solid precipitated. Work-up of the reaction mixture as described above gave benzoic anhydride (1.63 g, 72%) and **2** (2.49 g, 50%).

Reaction of Mercuric Succinate with Sulfenyl Chloride 5.—To a stirred suspension of mercuric succinate (3.17 g, 0.01 mol) in 20 ml of methylene chloride was added dropwise a reddish orange solution of **5** (2.90 g, 0.02 mol) in 10 ml of methylene chloride over a period of 20 min at room temperature. An immediate reaction took place as indicated by decolorization of **5**. A white precipitate of mercuric chloride (2.50 g, 92%) was collected by filtration. The filtrate was evaporated *in vacuo* to dryness and treated with ether. The resulting crystals of succinic anhydride (0.91 g, 91%), mp 117–118°, were filtered. The infrared spectrum was identical with that of an authentic sample. The filtrate was concentrated and chromatographed on alumina (80 g) to remove residual mercuric chloride. Elution with ether gave diphenyl disulfide (1.63 g, 75%), mp 59–60°.

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[9] All melting points and boiling points were uncorrected.

[10] T. Mukaiyama, H. Nambu, and I. Kuwajima, *J. Org. Chem.*, **28**, 917 (1963).

[11] W. W. Kaeding and A. T. Shulgin, *ibid.*, **27**, 3551 (1962).

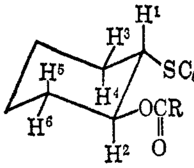
[12] R. A. Zingaro, J. E. Goodrich, J. Kleinberg, and C. A. VanderWerf, *J. Amer. Chem. Soc.*, **71**, 575 (1949).

[13] H. Lecher, *Chem. Ber.*, **48**, 1425 (1915).

[14] P. Noble, Jr., and D. S. Tarbell, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 924.

By a similar procedure, the other acid anhydrides were obtained from the corresponding mercuric and silver carboxylates (see Table II).

General Procedure for the Preparation of the Adducts (6–8).—To a stirred mixture of an olefin (0.02 mol) and a mercuric carboxylate (0.01 mol) in 20 ml of methylene chloride was added a solution of **5** (0.02 mol) in 10 ml of methylene chloride at room temperature over a period of 20 min. A slightly exothermic reaction took place soon. Stirring was continued for 20 min at room temperature. A white precipitate of mercuric chloride (1.8–2.2 g, 67–76%) was collected by filtration. The filtrate was concentrated and chromatographed on alumina (80 g) using ether as an eluent. After removal of ether, the residual oil was distilled to give the corresponding adduct. Yields, physical properties, and analytical data are listed in Table III. The infrared spectra of **6a**, **6b**, **7a**, **7b**, and **8** showed carbonyl absorptions at 1740, 1720, 1740, 1725, and 1740 cm^{-1}, respectively. The nmr[15] spectrum of **6a** showed peaks at τ 7.6–8.9 (complex, 8 H), 5.25 (sextet, 1 H, CH),[16] and 6.88 (sextet, 1 H, CH);[16] that of **6b** showed peaks at τ 7.6–8.9 (complex, 8 H), 5.01 (sextet, 1 H, CH),[16] and 6.71 (sextet, 1 H, CH).[16] The nmr spectrum of **7a** showed peaks at τ 6.73 (quartet, 1 H, CH_2),[17] 6.97 (quartet, 1 H, CH_2),[17] and 4.16 (quartet, 1 H, CH);[17] that of **7b** showed peaks at τ 6.57 (quartet, 1 H, CH_2),[17] 6.84 (quartet, 1 H, CH_2),[17] and 3.93 (quartet, 1 H, CH);[17] that of **8** showed peaks at τ 6.92 (doublet, 2 H, J = 6 cps, CH_2) and 4.13 (triplet, 1 H, J = 6 cps, CH).



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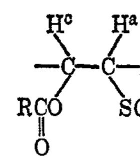

7, 8

Hydrolysis of 7b.—A solution of **7b** (3.34 g, 0.01 mol) and sodium hydroxide (0.60 g, 0.015 mol) in 25 ml of water and 25 ml of ethanol was heated on the steam bath for 10 hr. After removal of ethanol, the residue was diluted with 30 ml of water, extracted repeatedly with ether, and dried over anhydrous sodium sulfate. After removal of ether, the residual oil was distilled to give **9** (1.60 g, 70%): bp 138–139° (0.06 mm) [lit.[8] bp 168° (2 mm)]; ν_{max} 3410 (OH) cm^{-1}; nmr (CCl_4), two quartets centered at τ 7.00 (1 H) and 7.06 (1 H) with J_{ab} = 13 cps, a singlet at 6.45 (1 H, OH), a quartet at 5.48 (1 H, J_{ac} and J_{bc} = 5 and 8 cps), a multiplet centered at 2.88 (10 H, aromatic protons).

Anal. Calcd for $C_{14}H_{14}OS$: C, 73.02; H, 6.13. Found: C, 73.26; H, 6.00.

The aqueous, alkaline solution was acidified with dilute hydrochloric acid to give benzoic acid (1.00 g, 82%), mp 118–120°.

Reaction of Mercuric Thiobenzoate with 5.—To a stirred suspension of mercuric thiobenzoate (4.75 g, 0.01 mol) in 20 ml of methylene chloride was added a solution of **5** (2.90 g, 0.02 mol) in 10 ml of methylene chloride at room temperature. After stirring was continued for 10 min, a white precipitate of mercuric chloride (2.22 g, 82%) was filtered off. The filtrate was concentrated and distilled to give benzoyl phenyl disulfide[18] (3.96 g, 80%): bp 147–148° (0.1 mm); ν_{max} 1695, 1200, 885, 690, and 680 cm^{-1}.

Anal. Calcd for $C_{13}H_{10}OS_2$: C, 63.36; H, 4.09. Found: C, 63.65; H, 4.18.

Similarly, mercuric chloride (89%) and diphenyl disulfide (97%) were obtained from the reaction of mercuric benzenethiolate with **5**.

Reaction of Mercuric Benzenethiolate with 1.—To a stirred suspension of mercuric benzenethiolate (4.19 g, 0.01 mol) in 20 ml of methylene chloride was added **1** (2.96 g, 0.01 mol) at room temperature. A reaction took place immediately, and a clear yellow solution was formed. The reaction mixture was concentrated *in vacuo* to dryness and treated with ether. The yellow crystal of **2** (4.76 g, 95%), mp 134–136°, was collected by filtration. The filtrate was evaporated and chromatographed on alumina (80 g) to remove residual **2**. Elution with ether gave diphenyl disulfide (2.10 g, 98%), mp 59–60°.

Registry No.—**1**, 97-77-8; **2**, 16162-55-3; **5**, 931-59-9; **6a**, 16162-54-2; **6b**, 16162-48-4; **7a**, 16162-49-5; **7b**, 16162-50-8; **9**, 16162-51-9; benzoyl phenyl disulfide, 5718-98-9; mercuric thiobenzoate, 16162-53-1.

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[15] The nmr spectra were measured at 100 Mcps in CCl_4 solution with TMS as an internal standard, and these data were obtained by first-order analysis.

[16] $J_{12} = J_{14} = J_{25}$ = 8 cps, $J_{13} = J_{26}$ = 4 cps.

[17] J_{ab} = 14 cps, J_{ac} and J_{bc} = 6 and 8 cps.

[18] H. Böhme and M. Clement, *Ann.*, **576**, 61 (1952).

Steric Rate Enhancement in the Chapman Rearrangement

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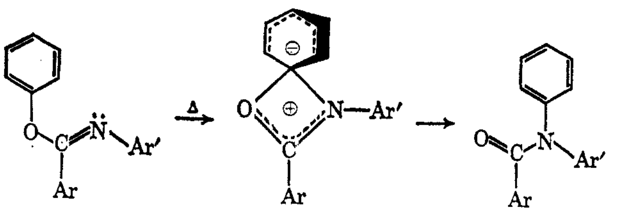
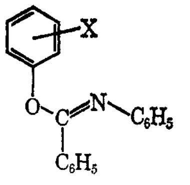
N-Phenylbenzimidates of 2,6-dimethyl-, 2,6-di-*t*-butyl-, 2,6-diphenyl-, and 2-methyl-6-phenylphenol have been prepared and have been found to undergo the Chapman rearrangement to give the corresponding N-arylbenzanilides. Kinetic measurements have been obtained and are discussed in terms of the competition between steric acceleration and steric deceleration of the rates of rearrangement.

An elegant study by Wiberg and Rowland[1] indicated that the Chapman rearrangement[2] obeyed first-order kinetics and that the mechanism involved an intramolecular, nucleophilic–aromatic substitution.



It was also reported[1] that the ratios of the rate constants for corresponding *ortho*- and *para*-substituted compounds (Ia–d) were greater than unity. It was assumed that the *ortho* substituent hindered free ro-



Ia, X = $CH(CH_3)_2$
b, X = CH_3
c, X = Cl
d, X = OCH_3
e, X = $C(CH_3)_3$
f, X = H

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[1] K. B. Wiberg and B. I. Rowland, *J. Amer. Chem. Soc.*, **77**, 2205 (1955).

[2] For a recent review, see J. W. Schulenberg and S. Archer, *Org. Reactions*, **14**, 1 (1965).