extracting with one 20-ml. and three 15-ml. portions of ether. The organic extract was washed with water and concentrated to dryness under reduced pressure. The deuterium content was determined by an infrared spectrophotometric method.[13] Weighed samples of recovered sulfone were dissolved in carbon tetrachloride (measured with a micro syringe) and spectra were determined with a Perkin-Elmer, single beam, double pass infrared spectrophotometer Model 112. The same 1.0-mm. sodium chloride cell was used for all of the determinations. Deuterium contents were determined from the intensity of the band near 10.8 μ with the aid of calibration curves[13] constructed from the spectra of synthetic mixtures. To check the method, samples determined to have 0.96, 0.43, and 0 atoms of deuterium per molecule by infrared spectroscopy were analyzed by combustion.[15] The combustion values were 0.967, 0.456, and 0.007. The results of an exchange experiment are shown in Table III.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

Reactions of Alkyl Carboxylic Esters with Mercaptides[1,2]

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A preliminary study of the scope and mechanism of the reaction between carboxylic esters and mercaptides is reported. The reactions were carried out under nitrogen, and in most cases involve attack by mercaptide at the alkyl carbon of the ester; however, with benzyl mercaptide a number of instances of acyl carbon attack were observed, especially where the alkyl carbon was hindered (*e.g.*, *t*-butyl, neopentyl). Since propyl mercaptide does not appear to attack propyl thiolbenzoate, and since the best evidence for effective acyl carbon attack is isolation of a symmetrical dialkyl sulfide formed from an intermediate thiol ester by further mercaptide attacking the alkyl carbon, it is concluded that acyl carbon attack by mercaptide on an ordinary ester is reversible, with the equilibrium favoring the normal ester. Thus when the irreversible formation of dialkyl sulfide is possible, acyl carbon attack as the apparent mode of reaction is observable; otherwise it is not.

The reaction between propyl mercaptide and methyl mesitoate and methyl benzoate has been shown to be a second-order process with an unusually high activation energy.

In connection with other studies in this laboratory it became desirable to investigate the possibility of using the reaction of alkali metal hydrogen sulfides with alkyl acylates as an extension of Kekulé's cleavage of phenyl acylates to phenol and potassium thioacylates.[3] The literature offered conflicting information: thus Wanklyn[4] reported that potassium hydrogen sulfide with ethyl acylates produced "no mercaptans" whereas others[5] have reported that mercaptans are produced. Preliminary work in our hands with sodium hydrogen sulfide and methyl benzoate indicated that the latter claim was correct, and that under all conditions only sodium benzoate (none of the thiol salt) could be produced. This intriguing preference for alkyl attack is in line with Reid's observation that hydrogen sulfide reacts with ethyl benzoate to give mercaptan and normal acid rather than the reverse of the reaction of benzoic acid with ethyl mercaptan which leads to ethyl thiolbenzoate.[6]

Consequently it was decided to see if this preference is general for anions derived from divalent sulfur, and to this end we focused our attention on mercaptides. Apart from the early observation of Seifert[7] that phenyl acylates are cleaved by sodium ethyl mercaptide to the expected ethyl thioacylates and sodium phenylate, all work involving mercaptides with carboxylic esters is of comparatively recent origin. Thus γ-lactones and β-lactones suffer alkyl attack,[8-11] but in one instance a specific β-lactone may experience acyl attack[11] as well. Furthermore, four reports,[12-15] one of which[15] appeared subsequent to initiation of the present work, suggest that alkyl attack by mercaptan or mercaptide may prevail in normal carboxylic esters as well as lactones; but the reported reactions all involve polyfunctional compounds. For example, β-mercaptoethanol diacetate is converted to ethylene sulfide on alkaline hydrolysis.[12] This implies preferential hydrolysis of the

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(2) Presented before the Organic Division of the American Chemical Society, 139th Meeting, St. Louis, Mo., March 21–30, 1961.

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TABLE I

REACTIONS OF ALKYL BENZOATES WITH MERCAPTIDES

$C_6H_5CO_2R + {}^{\ominus}SR'$

R/Moles[a]	Solvent/Ml.	Temp.[b]	Hr.	% Reaction	Product Isolated
R′ = H					
C_2H_5/0.5	None	213	24	90	$C_6H_5CO_2H$
R′ = propyl (I)					
C_2H_5/0.1	Ethanol/50	79	4.5	54	$C_6H_5CO_2H$
n-C_3H_7/0.2	Propanol/100	97	1.5	32	$C_6H_5CO_2H$
n-C_3H_7/0.1	Butanol/150	118	3	27	$C_6H_5CO_2H$[c]
i-C_3H_7/0.02	DMF/200	155	3	15	$C_6H_5CO_2H$
t-C_4H_9/0.02	DMF/200	155	4	16	$C_6H_5CO_2H$
t-C_5H_{11}/0.057	*N*-Methylacetamide/100	205	1	24	$C_6H_5CO_2H$
Cyclohexyl/0.1	Cyclohexanol/220	162	24	25	$C_6H_5CO_2H$
R′ = cyclohexylmethyl (IV)					
i-C_3H_7/0.02	DMF/200	155	3	16	$C_6H_5CO_2H$
R′ = benzyl (II)					
CH_3/0.02	DMF/200	155	3	35	$C_6H_5CO_2H$[d]
i-C_3H_7/0.2	DMF/300	155	5.75	—	$C_6H_5CH_2SCH(CH_3)_2$[e]
i-C_3H_7/0.02	DMF/200	155	3	14	$(C_6H_5CH_2)_2S$[e] (III)
t-C_4H_9/0.02	DMF/200	155	3	30	$(C_6H_5CH_2)_2S$[e] (III)
neo-C_5H_{11}/0.02	DMF/200	155	3	60	$(C_6H_5CH_2)_2S$[e] (III)

[a] Moles of mercaptide are same. [b] Reactions in nitrogen atmosphere at reflux. [c] Butyl propyl sulfide isolated as *p*-bromophenacylsulfonium picrate. [d] Benzyl methyl sulfide isolated in 35% yield as sulfone. [e] As sulfone.

TABLE II

REACTIONS OF MISCELLANEOUS ESTERS WITH MERCAPTIDES

Ester/Moles	Mercaptide/ Moles	Solvent/Ml.	Temp.	Hr.	% Reaction	Product
n-Amyl acetate/0.05	Benzyl/0.05	DMF/200	155	5	—	*n*-Amyl benzyl sulfide
Methyl mesitoate/0.011	Propyl/0.027	DMF/55	155	3	78	Mesitoic acid[b]
Propyl thiolbenzoate/0.04	Propyl/0.04	DMF/100	155	3.25	—	—[c]
Benzyl thiolbenzoate/ 0.015	Propyl/0.02	DMF/50	34	2.15	54	Propyl thiolbenzoate
Benzyl thiolbenzoate 0.05	Benzyl/0.05	DMF/200	155	6	41	Dibenzyl sulfide[a]

[a] As the sulfone. [b] Methyl propyl sulfide isolated as *p*-bromophenacylsulfonium bromide. [c] No detectable reaction.

thiolacetate to mercaptide followed by unimolecular displacement of normal acetate, which is somewhat puzzling, since Rylander and Tarbell have shown that simple alkyl acetates are more readily hydrolyzed in alkaline media than their thiol analogs.[16]

In the initial phases of our study we examined the behavior of a number of alkyl benzoates with two mercaptides, propyl (I) and benzyl (II), in various solvents, with attention being centered on the nature of the products (Table I). With I alkyl attack was invariable where any reaction could be detected; this was determined by isolation of benzoic acid and/or the unsymmetrical dialkyl sulfide, usually in the form of a derivative (*e.g.*, sulfonium salt or sulfone). With II, the usual product was dibenzyl sulfide (III), except for methyl and *n*-amyl benzoates which afforded unsymmetrical sulfides and benzoic acid.

The production of III suggested that initial formation of benzyl thiolbenzoate was followed by alkyl attack upon it, and the feasibility of the latter step was experimentally demonstrated (Table II). At the same time it was shown that propyl thiolbenzoate does not react with propyl mercaptide (Table II). With these data at hand the following reaction scheme offers a qualitative explanation for the observed facts:

$$C_6H_5CO_2R + {}^{\ominus}SR' \underset{}{\overset{(1)}{\rightleftharpoons}} C_6H_5COSR' + {}^{\ominus}OR$$

$$(2)\downarrow {}^{\ominus}SR' \qquad (3)\downarrow {}^{\ominus}SR'$$

$$C_6H_5CO_2{}^{\ominus} + RSR' \quad C_6H_5COS{}^{\ominus} + R_2'S$$

This is not unexpected since there is ample evidence to show that benzyl-*x*-compounds suffer displacement (S_N2) considerably faster than activated alkyl-*x* compounds.[17] The equilibrium constant, K_1, for reaction 1 is governed by the relative basicities of mercaptide and alkoxide and hence must be rather small; there will be a minor variation for different mercaptides (*e.g.*, larger for I, smaller for II) and alkoxides (*e.g.*, R = I° > R = II°

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TABLE III

INTERACTION OF SODIUM *n*-PROPYL MERCAPTIDE WITH ESTERS: REACTION RATE PARAMETERS

Ester	Temp.	Second-Order Rate Constant $\times 10^2$ (Alkyl Fission), L./Mole/Min.	Activation Energy, ΔE^*, Kcal./Mole	Activation Entropy, ΔS^*, Cal./Mole/Deg.	Log *PZ*
Methyl mesitoate	29.50 ± 0.06	5.33 ± 0.33[a]			11.65
	34.15 ± 0.05	12.20 ± 0.83[a]	32.9	−5.28	11.65
Methyl benzoate	29.50 ± 0.05	9.18			
Neopentyl benzoate	29.50 ± 0.05	[b]			
	34.15 ± 0.05	[b]			
Benzyl thiolbenzoate	34.15 ± 0.05	[c]			
(Blank)	29.50 ± 0.05	[b]			
(Blank)	34.15 ± 0.05	[b]			

[a] Average deviation from the mean. [b] No detectable reaction. [c] *n*-Propyl thiolbenzoate may have been formed; compare Table II.

> R = III°). The present investigation has shown that reaction 2 is first order in ester and in mercaptide; and while measurement of the rate of reaction 3 proved impossible, the similarity to reaction 2 suggests that reaction 3 is also first order in each reactant. Thus (unless the rate of reaction 1 is fast relative to that of reaction 2) the rates of all three reactions should be approximately equally sensitive to the concentration of mercaptide and so will depend primarily on the concentrations of ester (1 and 2) and thiol ester (3) and on the relative magnitudes of the respective rate constants, k_1, k_2, and k_3.

Since no reaction, even under forcing conditions, is observed between I and propyl thiolbenzoate, one may assume that for I, k_3 is vanishingly small [and likewise for cyclohexylmethyl mercaptide (IV)]. For II the following data permit approximate comparison of k_2 and k_3. The reaction of II with methyl benzoate *via* reaction 2 is 35% complete after three hours in refluxing dimethylformamide, while the reaction of II with benzyl thiolbenzoate *via* reaction 3 is 41% complete after 6 hr. under similar conditions. Thus for II and methyl benzoate it would appear that $k_2 > k_3$. The fact that the products of both reactions 2 and 3 can be obtained from II and isopropyl benzoate would seem to support the argument that the difference is not great, since the additional steric requirement of the secondary alkyl group should decrease k_2 somewhat and permit more successful competition by reaction 3. [That steric requirements in the mercaptide are not responsible for the observed difference in behavior of I and II is shown by the fact that IV, with approximately the same steric requirements as II behaves like I with ispropyl benzoate (Table I)].

The question of the relative magnitudes of the rate constants for reactions 1 and 2 can also be given a tentative answer. The invariable production of mercaptan and metal acylates from alkali metal hydrogen sulfides and alkyl acylates[5] (in all but the earliest report,[4] which may be safely disregarded) suggests that in the absence of strongly inhibitory steric or electronic effects the normal or preferred mode of attack of $^{\ominus}SR$ on a carboxylic ester is at the alkyl carbon. If this were not true, alkali metal hydrogen sulfides would be expected to produce the alkali metal thiolacylate and alcohol in spite of the small size of K_1 for the same reasons that hydroxide affords *complete* saponification in spite of a similarly unfavorable equilibrium constant. Thus it is most probable that $k_2 > k_1$. However, the reaction of propyl mercaptide with benzyl thiolbenzoate affords propyl thiolbenzoate, and in this instance it would appear that the rate of ester exchange is faster than attack at the alkyl carbon (analogous to reaction 3). The normal order (*i.e.*, for alkyl acylates and mercaptides) of rate constants thus is $k_2 > k_1 > k_3$.

When the free energy requirements of reaction 2 are raised (*e.g.*, R is secondary rather than primary), reaction 1 can compete successfully with it and provide a relatively mobile equilibrium. Under these conditions the rate expressions for reaction 2 and 3 are

$$V_2 = k_2[\text{ester}][^{\ominus}\text{SR}']$$

$$V_3 = k_3'[\text{ester}]^{1/2}[^{\ominus}\text{SR}']^{1/2}$$

where all concentrations are those for reaction 1 at equilibrium and $k_3' = k_3 \times K_1^{1/2}$. Thus with a decrease in k_2 and no change in k_3, the rate of reaction 3 is enhanced by a factor of $K_1^{1/2}$ (and by any increase in mercaptide concentration relative to ester). Consequently it is not surprising that a change in R from primary to secondary to tertiary or neopentyl should be reflected by increasing yields of III (dibenzyl sulfide) under similar incomplete reaction conditions.

Such conclusions as are available from this preliminary survey may be summarized as follows: When a mercaptide reacts with an alkyl acylate and the mercaptide is nonbenzyl in character, attack will be on the oxygen-alkyl carbon of

the ester unless this is so sterically hindered (*e.g.*, neopentyl) to prevent normal S_N2 reactions at this site; if a benzyl-type mercaptide is used, attack will normally be at the acyl carbon of the ester unless the alkyl group is primary, when alkyl attack will occur. Secondary alkyl groups will permit some selectivity, owing to the relationship between the rate constants of the reaction scheme given above; thus alkyl attack will be favored by a concentration of ester higher than that of mercaptide.

Direct comparison of rate data for alkyl-oxygen ester cleavage by alkoxide and mercaptide is not possible, but the following observations are significant. The reaction of I with methyl mesitoate in dimethylformamide (ester 0.05*M*), mercaptide 0.09*M*) is 38% complete at 29.5° in two hours, while the reaction with methoxide in methanol at 100° is only 4% complete after four hours.[18] Consequently the rate constant for the former type of reaction must be very much smaller.

A final piece of evidence is enlightening. In an attempt to carry out reaction 2 between propyl benzoate and I in butanol at 118° the product obtained was *butyl* propyl sulfide rather than dipropyl sulfide. Thus ester exchange (catalyzed presumably by butoxide ion formed in very low concentration by metathesis) is considerably faster than attack of mercaptide at the alkyl carbon of the ester. (This observation casts doubt on the claim of an early paper[5a] that *n*-amyl butyrate and isoamyl acetate in ethanol at 180° yield the amyl mercaptans with potassium hydrogen sulfide.) There does not appear to be any data on alkoxide catalyzed ester exchange rates, but this evidence suggests that they are faster than our reaction 1, since the one in question is evidently much faster than our reaction 2.

Thus we have the following situation: mercaptide (and $^{\ominus}SH$) prefers alkyl attack, even though the activation energy is very high (33 kcal./mole) and the other mode of reaction is open to it; but alkoxide prefers carbonyl attack. Furthermore, the rate of the latter reaction is greater than the rate of mercaptide (and $^{\ominus}SH$) attack on carbonyl. Swain and Scott[19] have offered a reasonable and very nearly explicit explanation for the latter condition by pointing out that with hydroxide ion and an ester considerable charge distribution is gained in the transition state which is not realized with the more polarizable sulfur anion. Conversely, formation of the transition state for acylate displacement by sulfur anion should be easier than for oxygen anion, since the greater polarizability of sulfur permits more facile approach to the alkyl carbon.

The Swain-Scott argument, however, does not venture a comparison of activation energies of two different transition states formed from the same substrate and nucleophile, beyond pointing out the well documented competition between E2 and S_N2 reactions in the same medium. Since the latter can be influenced by medium changes, one would expect the same to be observed in the ester-mercaptide reaction. Unfortunately, thus far the one instance of this occurs with a β-lactone,[11] for which precedents have established a pattern of *p*H-dependent behavior. But it is perhaps significant that alkyl attack on the β-lactone occurs in alcohol while acyl attack occurs in water, which suggests that there are greater charge repulsions to be overcome in forming the transition state for acyl attack, and that solvation factors may play an important role. Consequently one might expect the entropy of activation to have considerable significance in promoting alkyl attack over acyl attack.

It is not possible to determine reaction parameters for acyl attack of mercaptide on an alkyl benzoate, as shown by complete failure to detect reaction between neopentyl benzoate and I; any attempt to get at them by using II very probably would lead only to values for reaction 3. However, the reaction between phenyl benzoate and I might permit an approximate comparison. Unfortunately the analytical problem has thus far precluded obtaining rate data for this reaction, but we hope to obtain it later. In any case it would seem that one may be able to attribute the preference for alkyl attack to the less stringent steric requirements for this mode of reaction arising from the polarizability of sulfur and solvation effects.

EXPERIMENTAL[20]

Materials. The following reagents were prepared according to published procedures or modifications thereof: sodium hydrogen sulfide[21]; cyclohexyl mercaptan[22]; cyclohexylmethyl mercaptan[22]; b.p. 65.5–66.0°/8 mm.

Anal. Calcd. for $C_7H_{14}S$: C, 64.55; H, 10.83. Found: C, 64.31; H, 10.79 (Spang Microanalytical Laboratory, Ann Arbor, Mich).

Benzyl methyl sulfide[23]; benzyl isopropyl sulfide[23]; dibenzyl sulfide[24]; *n*-amyl benzyl sulfone (from *n*-amyl mercaptan and benzyl chloride followed by oxidation[25] of crude sulfide)[23]; benzyl methyl sulfone (oxidation of sulfide)[25]; benzyl isopropyl sulfone (oxidation of sulfide)[25]; dibenzyl sulfone (oxidation of sulfide)[25]; cyclohexyl propyl sulfone (from cyclohexyl mercaptan and propyl bromide followed by

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oxidation[25] of the crude sulfide)[26]; *t*-amyl benzoate[27]; *t*-butyl benzoate[28]; cyclohexyl benzoate[29]; neopentyl benzoate[30]; propyl and isopropyl benzoates by Fischer esterification; methyl mesitoate[31]; benzyl thiolbenzoate[32]; propyl thiolbenzoate.[33]

Ethyl benzoate and sodium hydrosulfide. To 75 g. (0.50 mole) of freshly distilled ethyl benzoate placed in the apparatus described below was added 5.6 g. (0.10 mole) of sodium hydrosulfide and the reactants were refluxed for 24 hr. in an atmosphere of nitrogen. At the end of this time a considerable amount of solid had separated and bumping was quite severe. After cooling the reaction vessel, the salt was dissolved in water, treated with Norit, filtered, and the filtrate was acidified with concd. hydrochloric acid. The benzoic acid was isolated by extracting this acidic solution with carbon tetrachloride and evaporating the solvent under an air stream. A total of 11.0 g. (90%), m.p. and mixed m.p. 120–121°, was obtained.

Reactions of esters with mercaptides. A three-neck round-bottom flask of suitable volume carrying a sealed stirrer, condenser attached to a mercury trap, and a fitting consisting of a Pyrex tube with joint at lower end and constricted at upper end to fit a rubber serum-bottle stopper which was secured by wiring to hooks on the glass. A stopcock which served as inlet tube was joined into this fitting just below the upper end.

Before introduction of the solvent the apparatus was flamed out while being flushed with a slow stream of dry nitrogen. After cooling to room temperature the solvent and sodium were introduced, the system again flushed with nitrogen and the inlet closed. When the solvent was an alcohol, the sodium was allowed to dissolve before addition of mercaptan; otherwise the mercaptan was immediately injected through the stopper from a syringe and the mercaptide was prepared *in situ* with stirring and heating. Upon disappearance of the sodium the ester was injected from a syringe, and the reaction time was measured as of completion of this operation. The work-up varied with isolation requirements; typical procedures follow.

Methyl mesitoate and propyl mercaptide in N,N-dimethylformamide. The reaction was carried out in 50 ml. of dry dimethylformamide using 0.63 g. (0.027 g.-atom) of sodium, 2.5 ml. (0.028 mole) of propyl mercaptan, and 2.0 g. (0.011 mole) of methyl mesitoate in 5 ml. of dimethylformamide. The mixture was refluxed for 3 hr. and then cooled. A small Vigreux column was then attached, and the distillate from 75–145° was collected and dissolved in 5 ml. of absolute methanol. This solution was refluxed for 1 hr. after addition of 1.5 g. (0.0054 mole) of *p*-bromophenacyl bromide. After cooling 200 ml. of absolute ether was added whereupon a precipitate appeared. After standing at 0° for 1 hr., the mixture was filtered, washed with dry ether and air dried. The product was propyl-*p*-bromophenacylsulfonium bromide, 1.05 g. (26%). After recrystallization by solution in methanol and precipitation with ether (3 times) it melted at 101.7–103.9°, reported[34] 109.5°.

The residue from the original distillation afforded 1.42 g. (78.5%) of mesitoic acid, m.p. and mixed m.p. 150–154°, after dilution with water, ether extraction, extraction of the ether with sodium hydroxide (10%) precipitation with hydrochloric acid and filtration after cooling to 10°. The precipitate was washed with water and petroleum ether (b.p. 40–60°).

Ethyl benzoate and propyl mercaptide in ethanol. Sodium (2.3 g., 0.10 g.-atom) and absolute ethanol (50 ml.) were allowed to react completely and then 9.4 ml. (0.10 mole) of propyl mercaptan was added, followed by 15 g. (0.10 mole) of ethyl benzoate. The mixture was refluxed for 4.5 hr. and then allowed to stand overnight. The resultant precipitate was filtered off and washed with 250 ml. of dry ether, and the filtrate was distilled to dryness. The residues from filtration and distillation were combined and dissolved in 200 ml. of water, extracted twice with ether, and the aqueous layer was acidified to Congo red. Benzoic acid was isolated by two 100-ml. extractions with carbon tetrachloride and evaporation of the extracts to dryness: 6.5 g. (54%); identified by mixed melting point.

Propyl benzoate and propyl mercaptide in butanol. The reaction was carried out as in the previous experiment (*cf.* Table I for quantities of reagents.) A dense precipitate of sodium benzoate caused severe bumping after 3 hr. Benzoic acid was recovered by filtration, solution of residue in water, and acidification (27%). The filtrate was diluted with 100 ml. of water and 75 ml. of ether, separated, and the ether dried over magnesium sulfate. The ether and butanol were the distilled and the residue was dissolved in 5 ml. of reagent methanol, treated with 2.8 g. (0.010 mole) of *p*-bromophenacyl bromide and refluxed for 1 hr. After cooling, dilution with 200 ml. of ether, and standing overnight at 0° the crude sulfonium bromide was filtered off, dissolved in water, and treated with a saturated aqueous solution of picric acid. The resultant salt was recrystallized from aqueous ethanol from which the product was isolated by refrigerating the supernatant liquid removed by decantation from a gummy precipitate. The propylbutyl-*p*-bromophenacylsulfonium picrate melted at 76–78°, reported[34] 77–78°. Identity was confirmed by analysis.

Benzyl thiolbenzoate and sodium n-propyl mercaptide in N,N-dimethylformamide. Fifty milliliters of a 0.43*M* solution (0.022 mole) of sodium *n*-propyl mercaptide in dimethylformamide was added to 3.42 g. (0.0150 mole) of benzyl thiolbenzoate in the reaction vessel used for kinetic determination (see below). An atmosphere of nitrogen was introduced, and the resulting solution was allowed to stand in a thermostat at 34.15 ± 0.05° for 2 hr. and 10 min. The reaction mixture was then poured into 100 ml. of ether, and the vessel was rinsed into the ether with about 20 ml. of water. The two layers were separated, and the aqueous portion was extracted three times, using 50 ml. of ether each time. The combined ether extracts were treated three times with 50-ml. volumes of water. The ether extracts were then dried using sodium sulfate and magnesium sulfate, and the solvent was removed by distillation, leaving 2.9 g. of a cloudy residue, which was distilled at reduced pressure, yielding 1.45 g. (54%), b.p. 164–170°/47 mm., identified as *n*-propyl thiolbenzoate by the identity of its infrared spectrum with that of the authentic thiol ester.

Kinetic determinations. Materials. Methyl benzoate was Eastman Kodak White Label, twice redistilled. Methyl mesitoate: b.p. 70–72°/0.7 mm., $n_D^{23.5}$ 1.5075. Neopentyl benzoate was an analytical sample: b.p. 42–43°/0.1 mm., $n_D^{26.5}$ 1.4874. *N,N*-Dimethylformamide was Du Pont technical grade which was dried by refluxing for 12 hr. over calcium hydride, then distilled from calcium hydride through a six cap bubble-cap column, b.p. 151–152°.

Solutions of the esters were prepared by dissolving accurately weighed quantities in dry, distilled *N,N*-dimethylformamide and diluting quantitatively. Concentrations were of the order of 0.1*M*. Since equal volumes of the ester and the mercaptide stock solutions were used, the initial concentrations were easily determined and fell within the range 0.0460*M* to 0.0510*M* for all esters.

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A typical preparation of a stock solution of sodium *n*-propyl mercaptide is described below. This solution was diluted to approximately twice the initial concentration desired for the kinetic experiments and analyzed iodametrically immediately preceding each run. Initial concentrations under reaction conditions could then be calculated as for the esters. Specifically, these ranged from 0.0700*M* to 0.1070*M* for the reactions involving methyl mesitoate and methyl benzoate as substrates, and from 0.1280*M* to 0.1370*M* for neopentyl benzoate, while the initial mercaptide concentration ranged from 0.0800*M* to 0.1000*M* for the blanks which were run on the sodium n-propyl mercaptide solution alone.

A two-piece glass reaction vessel was used. The cap consisted of a 45/50 standard taper joint which was closed at the top, then fitted with inlet and outlet tubes for nitrogen both of which bore stopcocks. A short length of 14 mm. tubing with a 14/35 standard taper joint at the upper end projected vertically and served as a sample port. During kinetic runs this opening was closed by a 14/35 standard taper stopper held in place by a spring clamp. The other part consisted simply of a 45/50 standard taper joint which was closed off about 2 in. from the lower edge of the joint, thereby forming a flask of approximately 75 ml. capacity. Hooks were attached to both halves, which were held together by springs.

The reaction vessel was assembled and dried at 120° for 15 min. It was then fitted with a calcium chloride tube, and allowed to cool to room temperature. The vessel was placed in a thermostat, the outlet tube was attached to a mercury valve, and nitrogen was introduced through the inlet tube. After an inert atmosphere had been created, the nitrogen flow was stopped, except as the stopper was removed from the sample port during pipetting of samples. The vessel was then stoppered, flushed briefly with nitrogen as before, and the two stopcocks were close. When samples for analysis were removed the procedure used was the same as that described for the introduction of reactants.

All reaction rates were followed by analyzing for sodium *n*-propyl mercaptide. A 2-ml. sample was removed by pipette and added to 5 ml. of standard 0.1*N* iodine solution in 10 ml. of acetate buffer (0.05*M* in sodium acetate and in acetic acid). The excess iodine was titrated with 0.015*N* standard sodium thiosulfate.

Experiments were carried out on a qualitative basis which showed that sodium *n*-propyl mercaptide reacts with methyl mesitoate to yield methyl *n*-propyl sulfide and mesitoic acid, and with methyl benzoate to produce methyl *n*-propyl sulfide and benzoic acid.

Sodium propyl mercaptide in N,N-dimethylformamide. The salt was prepared in a nitrogen atmosphere from 2.22 g. (0.0967 g.-atom) of sodium and 11.5 ml. (0.127 mole) of propyl mercaptan in 80 ml. of dry xylene (distilled from calcium hydride).[35] After cooling in a nitrogen atmosphere, the mixture was poured into 400 ml. of dry ether, held at 0° for 0.5 hr., and filtered on a fritted glass funnel. The residue was washed well with dry ether and dried *in vacuo* over calcium chloride for 0.5 hr. The dry salt was then dissolved in 170 ml. of dry dimethylformamide, and the concentration was determined iodimetrically (0.4483*M*); yield 80%.

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Cyclopentene-3,5-dione. IV. Reaction with Brominating Agents and with Ethanol[1,2]

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Cyclopentene-3,5-dione has been shown to react with a variety of halogenating agents, each one giving predominately a different halogenation product. Reaction with bromine in carbon tetrachloride proceeded by addition and substitution to give 2,4,5-tribromocyclopentane-1,3-dione while *N*-bromosuccinimide gave mainly 4,4-dibromocyclopentene-3,5-dione and 1,4,4-tribromocyclopentene-3,5-dione. Addition of the dione to a solution of bromine in aqueous sodium bicarbonate furnished 4,4-dibromocyclopentene-3,5-dione in satisfactory yields. The enedione also reacted smoothly with ethyl alcohol in the presence of boron trifluoride to form 3,4-diethoxycyclopent-2-enone. This compound could be reduced and hydrolyzed to 5-ethoxycyclopent-2-enone.

A few years ago we developed a synthesis of the interesting and unusual compound cyclopentene-3,5-dione (I),[3] a stable, yellow solid which easily undergoes a large number of reactions, including condensations, reductions, derivatizations, and Diels-Alder additions. In general, it seems fair to say that there are almost no methods currently available for the synthesis of a vast number of simply substituted unsaturated cyclopentane derivatives, and we have been exploring the chemistry of cyclopentene-3,5-dione and of cyclopentenone,[4] as these molecules appear to be the most likely precursors for many other cyclopentane compounds. In this paper we report on the reactions of the dione with various brominating agents and with ethyl alcohol. All of these reactions lead to potentially useful synthetic intermediates, and some of them have interesting theoretical implications.

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