Acyl–Oxygen *versus* Aryl–Oxygen Bond Scission in Reactions of Benzenethiolate with Nitrophenyl Esters of Carboxylic Acids

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A number of nitrophenyl esters of acetic and benzoic acid have been found to undergo both carbonyl carbon–oxygen and aryl carbon–oxygen scission in reaction with sodium benzenethiolate in ethanol. The ratio of C_{CO}–O to C_{Ar}–O scission has been determined for the reactions of eight ester substrates: *o*-nitrophenyl acetate (ONPA), *o*-nitrophenyl benzoate (ONPB), *p*-nitrophenyl acetate (PNPA), *p*-nitrophenyl benzoate (PNPB), 2,4-dinitrophenyl acetate (2,4-DNPA), 2,4-dinitrophenyl benzoate (2,4-DNPB), 2,6-dinitrophenyl benzoate (2,6-DNPB), and 2,4,6-trinitrophenyl benzoate (2,4,6-TNPB). The fraction of C_{CO}–O scission varies according to the substrate from 100% for the mononitrophenyl esters to 0% for 2,4,6-TNPB. The overall rate constants k_{tot} for the reactions of these esters with sodium benzenethiolate have also been measured spectrophotometrically (u.v.) in ethanol at 22°; k_{tot} was separated into two composite rate constants k_{CO} and k_{Ar} corresponding to the cleavage of C_{CO}–O and C_{Ar}–O bonds respectively. k_{CO} increases in the series ONPB < PNPB < ONPA < 2,6-DNPB $\leqslant$ PNPA < 2,4-DNPB < 2,4-DNPA and k_{Ar} in the series 2,6-DNPB < 2,4-DNPA < 2,4-DNPB < 2,4,6-TNPB. Both k_{CO} and k_{Ar} decrease with increasing ionic strength. The reactions of 2,4-DNPA and of 2,4-DNPB with sodium benzenethiolate show a decrease of both k_{CO} and k_{Ar} on changing the solvent from ethanol to methanol, the solvent effect being slightly more pronounced for Ar than for CO attack.

THE widely recognized importance of thiol esters as intermediates in biochemical reactions[1] and, on the other hand, the paucity of information about the nucleophilicity of thiols towards an ester carbonyl carbon atom,[2] have prompted us to gain further insight into the details of the reaction of phenolic esters of carboxylic acids with thiols.

We have already reported[2] a kinetic study of the nucleophilicity of substituted arenethiolates in reactions with *p*-nitrophenyl acetate (PNPA). The present experiments were undertaken in an attempt to investigate the effect of variation in the leaving group on the rate of the reactions of nitrophenyl esters of carboxylic acids with benzenethiolate. However, an interesting complication was encountered when a second nitro-group was introduced into the phenolic moiety of PNPA. We found that in the reaction of 2,4-dinitrophenyl acetate (2,4-DNPA) other products were formed beside the expected 2,4-dinitrophenol (2,4-DNP) and *S*-phenyl thioacetate. Isolation and identification of products suggested that a significant fraction of the reaction of 2,4-DNPA proceeds with attack by benzenethiolate on C-1 of the aromatic ring to give 2,4-dinitrophenyl phenyl sulphide by nucleophilic aromatic substitution.

This was a somewhat surprising result since for aryl esters of carboxylic acids mostly acyl–oxygen fission takes place.[1,3] Aryl–oxygen fission is reported only for the neutral methanolysis of 2,4,6-trinitrophenyl benzoate (2,4,6-TNPB)[4] and for the reaction of PNPA with piperidine in dimethyl sulphoxide.[5] On the other hand, the nucleophilic substitution reactions of nitrophenyl sulphonates,[6] sulphates,[7] and phosphates,[8] in which competition arises between two electrophilic centres in the same ester substrate, are well documented.

In view of these facts it seemed to us of obvious interest to gain information about the occurrence of C_{CO}–O *versus* C_{Ar}–O bond cleavage in the reaction of phenolic esters of carboxylic acids with thiols and about the factors affecting the mode of scission. In this paper we report a kinetic study of the reactions of various nitrophenyl esters of acetic and benzoic acid with sodium benzenethiolate in 95% ethanol at 22°. The effects of solvent and of ionic strength are also described. Some of the data have been reported in preliminary form.[9]

RESULTS

The reaction of 2,4-DNPA with sodium benzenethiolate can be represented as in the Scheme. The attacking sites of the ester are both the carbonyl carbon atom (C_{CO}–O bond cleavage) and the dinitrophenyl carbon atom (C_{Ar}–O bond cleavage). C_{CO}–O Scission (route a) leads to sodium 2,4-dinitrophenolate and to *S*-phenyl thioacetate, while C_{Ar}–O scission (route b) leads to 2,4-dinitrophenyl phenyl sulphide and sodium acetate. The direction of fission was established as described in the Experimental part.

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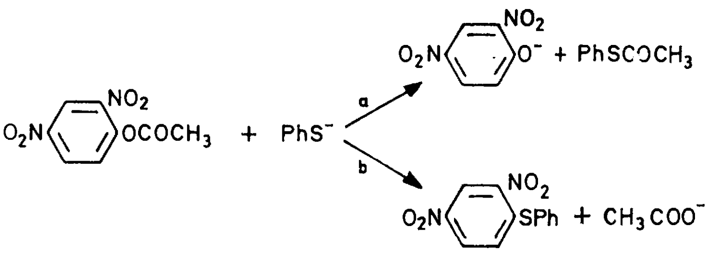
Table 1 summarizes the results for the reaction of benzenethiolate with 2,4-DNPA in ethanol at 22° at different concentrations of substrate, thiol, and thiolate. The rate of the reaction was followed by observing the increase of optical density near 340 nm due to the formation of 2,4-DNP and 2,4-dinitrophenyl phenyl sulphide. The overall rate constant k_{tot} was split into k_{CO} (rate of C_{CO}–O bond cleavage) and k_{Ar} (rate of C_{Ar}–O bond cleavage) by multiplying the second-order coefficient by the experimentally determined fractions of C_{CO}–O and C_{Ar}–O scission, respectively.



SCHEME

The variation of k_{obs} and constancy of k_{tot} with changing [PhS$^-$] indicate that the thiolate anion is the sole reactive species in the rate-determining step and that the reaction is first order in benzenethiolate anion. A variation in [PhSH] has no significant effect on the rates, thus showing that no catalysis by benzenethiol is operating. The slight decrease in k_{tot} (and k_{CO} and k_{Ar}) with a two-fold increase in [PhS$^-$] may be due to ionic salt effects, as shown by runs with solutions adjusted to different ionic strengths by addition of lithium chloride (see Table 2).

TABLE 1

Reaction of 2,4-DNPA with benzenethiolate in ethanol at 22°

10^5[2,4-DNPA]/M	10^4[PhSH]$_{\text{total}}$/M	10^4[PhSH]$_{\text{free}}$/M	10^4[PhS$^-$]/M	10^2k_{obs} [a]/s^{-1}	k_{tot} [b]/l mol^{-1} s^{-1}	%C_{CO}–O [c] scission	k_{CO} [b]/l mol^{-1} s^{-1}	k_{Ar} [b]/l mol^{-1} s^{-1}
1.00	32.00	30.03	1.97	1.302	66.09	48.3	31.92	34.17
1.00	41.50	39.56	1.94	1.284	66.19	48.2	31.90	34.29
1.00	62.00	60.05	1.95	1.287	66.00	48.5	32.01	33.99
1.00	34.06	30.10	3.96	2.594	65.51	48.7	31.90	33.61
2.03	64.06	60.05	4.01	2.621	65.36	48.0	31.37	33.99

[a] k_{obs} is total pseudo-first-order rate constant for all reactions consuming substrate. [b] k_{tot}, k_{CO}, and k_{Ar} are, respectively, second-order rate constants for the sum of C_{CO}–O and C_{Ar}–O cleavage, and for C_{CO}–O and C_{Ar}–O cleavage separately. [c] The figures listed are the spectrophotometrically (u.v.) determined percentage of C_{CO}–O scission; subtraction from 100% gives the percentage of C_{Ar}–O scission.

Table 2 reports the nature of the cleavage and the rate constants for the reaction of sodium benzenethiolate with a variety of nitrophenyl esters of acetic and benzoic acid, *i.e.*, PNPA, *p*-nitrophenyl benzoate (PNPB), *o*-nitrophenyl acetate (ONPA) and benzoate (ONPB), 2,4-DNPA, 2,4-dinitrophenyl benzoate, (2,4-DNPB), 2,6-dinitrophenyl benzoate (2,6-DNPB), and 2,4,6-TNPB.

The behaviour of 2,4-DNPA towards sodium ethoxide in ethanol at 22° was also studied. Although this reaction was too fast to be followed by the technique we used, product isolation experiments and spectrophotometric (u.v.) analysis showed that total acyl–oxygen fission occurred, yielding 2,4-DNP and ethyl acetate.†

DISCUSSION

The most significant discovery in this research is that simultaneous acyl–oxygen and aryl–oxygen scission occurs when sodium benzenethiolate reacts with 2,4-DNPA in ethanol. In fact, Jencks and Gilchrist [10] reported that a series of oxyanion nucleophiles ranging from methoxyacetate ion to hydroxide ion (conjugate acid pK_a values from 3.4 to 15.75) reacted with 2,4-DNPA in aqueous solution with typical carbonyl displacement reaction. Furthermore, the reaction of sodium ethoxide with 2,4-DNPA in ethanol proceeds with total acyl–oxygen fission, as we have shown.

An explanation of this behaviour may be given in terms of polarizability, whose importance as a component of nucleophilic character has received support.[11] Bunnett [12] has noted that reaction rates are usually fast when a nucleophile of high polarizability reacts with a substrate carrying a highly polarizable substituent at or near the reaction site. This was attributed to stabilization of the transition state by London forces.

The vicinity of C-1 of the phenol moiety of 2,4-DNPA is probably a region of higher effective polarizability than that of the carbonyl function of the ester. The short range nature of London forces supports the differentiation, in spite of their proximity, of the two electrophilic centres in the same substrate. Such forces, in fact, depend on the product of the polarizabilities of the interacting groups and vary inversely with the sixth power of the distance between them.[13]

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† The matter is under investigation and will be reported later.

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It is likely that, as suggested by other authors,[6a] the 2-nitro-group is a major contributor to high polarizability in the region of C-1 of the phenol moiety. In terms of the ' hard and soft acids and bases ' principle[14] the carbonyl carbon of the ester would be a ' hard ' acid centre, while the dinitrophenyl carbon would be a ' soft ' acid centre. A reagent of high polarizability such as the benzenethiolate ion, which is ' soft,' is therefore inclined to attack the dinitrophenyl carbon atom with occurrence of C_{Ar}–O scission, favourable London forces being operative between the reagent and the carbon atom. Ethoxide anion, on the contrary, which is known to be a harder base than benzenethiolate anion, is inclined to attack the ' hard ' electrophilic centre provided by the carbonyl carbon, with occurrence of (total) C_{CO}–O scission.

TABLE 2

Reactions of sodium benzenethiolate with esters at 22° [a]

Ester	I/M [b]	k_{tot} [c]/ l mol^{-1} s^{-1}	%C_{CO}–O [d] scission	k_{CO} [c]/ l mol^{-1} s^{-1}	k_{Ar} [c]/ l mol^{-1} s^{-1}
ONPA	0.5	3.78×10^{-2}	100	3.78×10^{-2}	
ONPB	0.5	4.15×10^{-3}	100	4.15×10^{-3}	
PNPA	0.5	19.8×10^{-2}	100	19.8×10^{-2}	
	0.05 [e]	23.7×10^{-2}	100	23.7×10^{-2}	
	0.01 [e]	25.4×10^{-2}	100	25.4×10^{-2}	
PNPB	0.5	2.11×10^{-2}	100	2.11×10^{-2}	
	0.05	2.35×10^{-2}	100	2.35×10^{-2}	
	0.01	2.60×10^{-2}	100	2.60×10^{-2}	
2,4-DNPA	0.5	43.75	48.3	21.13	22.62
	0.1	52.48	47.9	25.14	27.34
	0.05	57.00	48.8	27.82	29.18
	0.01	61.05	48.0	29.30	31.75
	0.000 2 [f]	66.09	48.3	31.92	34.17
	0.5 [g]	9.28	56.8	5.27	4.01
2,4-DNPB	0.5	48.63	15.8	7.68	40.95
	0.1	57.72	16.0	9.24	48.48
	0.05	64.00	16.7	10.69	53.31
	0.01	68.69	16.2	11.13	57.56
	0.000 2 [f]	74.14	15.8	11.71	62.43
	0.5 [g]	8.90	24.3	2.16	6.74
2,6-DNPB	0.5	1.66	10.4	0.17	1.49
	0.05	2.10	10.6	0.22	1.88
	0.006	2.50	10.4	0.26	2.24
	0.002	2.61	10.5	0.27	2.34
2,4,6-TNPB [h]			0		

[a] Solvent 95% ethanol, if not otherwise specified. [b] Where necessary, ionic strength adjusted to the required value by addition of lithium chloride. [c] See footnote *b*, Table 1. [d] See footnote *c*, Table 1. [e] Values taken from ref. 2. [f] Ionic strength was 0.000 2M in the buffers used for kinetics and 4×10^{-3}M in the buffers used for determinations of %C_{CO}–O scission. [g] Methanol used as solvent. [h] The reaction was too fast to be followed by the technique we used.

There exists a strong resemblance between our observations and those of Bunnett *et al.*[6a] They have shown that 2,4-dinitrophenyl toluene-*p*-sulphonate undergoes prevailing C–O scission by some reagents and prevailing S–O scission by others. They observed that very basic nucleophiles preferred to attack tetrahedral sulphur (which can be compared with the carbonyl carbon of carboxylic esters) whereas more polarizable ones attacked the aromatic carbon atom.

Another noteworthy result which has emerged is that sensitive changes of the degree of C_{CO}–O scission occur with changing the number of nitro-groups in the phenol moiety of the esters. Thus, whereas the mononitrophenyl esters undergo (I 0.5M; ethanol) total C_{CO}–O scission by benzenethiolate, 2,4-DNPA and 2,4-DNPB are cleaved in this manner only to the extent of 48.3 and 15.8%, respectively. The fraction of C_{CO}–O scission drops to *ca.* 10% with 2,6-DNPB and, finally, 2,4,6-TNPB is totally cleaved by benzenethiolate ion with C_{Ar}–O scission. The different sensitivity of the two reaction centres to the electronic effect of the substituent in the phenol moiety of the esters may be responsible for the observed behaviour. In fact, the rates of both C_{CO}–O and C_{Ar}–O scission would be predicted to be decreased by removal of one nitro-group from the phenol moiety, since both reactions are assisted by electron withdrawal from the reaction sites. Of the two reactions, however, C_{Ar}–O scission would be expected to be the more sensitive to polar substituent effects in the phenolic ring, on the basis of the fact that the Hammett ρ values for aromatic nucleophilic substitutions in substituted halogenonitrobenzenes (*ca.* +4)[3a,15] are significantly higher than those reported (*ca.* +1.7, +1.9)[3a,16] for nucleophilic attack on the ester carbonyl function in phenyl-substituted acetates

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and benzoates. Thus, removal of a nitro-group from or introduction of a nitro-group into the phenol moiety of the dinitrophenyl esters was expected to cause a decrease or an increase, respectively, in the fraction of C_{Ar}–O scission, as borne out by the results.

The rate coefficients for the reactions of the various esters with sodium benzenethiolate were found to depend on the ionic strength of the solution. Thus, k_{tot} for the reactions of benzenethiolate with both 2,4-DNPB and 2,4-DNPA decreases *ca.* 40% with a 50-fold increase in ionic strength (from 0.01 to 0.5M), as shown in Table 2. It is noteworthy that the ratio of C_{CO}–O to C_{Ar}–O scission is little influenced by variation of ionic strength, and that the changes in the percentage of C_{CO}–O bond cleavage, if any, are quite randomly distributed; this means that the effect of changing ionic strength is nearly the same on both acyl–oxygen and aryl–oxygen fission. The data displayed in Table 2 indicate that the rate constants for all esters show substantially the same dependence on ionic strength. We have therefore considered it justifiable to compare rate constants at one ionic strength, 0.5M, rather than extrapolate the rate data to zero ionic strength.

Inspection of the rate coefficients, determined at an ionic strength of 0.5M, in ethanol at 22° (Table 2) shows that for carbonyl carbon attack the sequence is ONPB $<$ PNPB $<$ ONPA $<$ 2,6-DNPB $\leqslant$ PNPA $<$ 2,4-DNPB $<$ 2,4-DNPA, while for aryl carbon attack the sequence is 2,6-DNPB $<$ 2,4-DNPA $<$ 2,4-DNPB $<$ 2,4,6-TNPB. Some points are revealed from comparison of the results in Table 2. (a) The rate of carbonyl attack by benzenethiolate is higher for the acetates than for the benzoates. In the case of the mononitrophenyl esters an approximately nine-fold increase in reactivity is observed on passing from ONPB and PNPB to ONPA and PNPA, respectively; in the case of the dinitrophenyl esters the increase in k_{CO} is approximately three-fold on going from 2,4-DNPB to 2,4-DNPA. This is the expected behaviour since the acetyl group is well known to be more reactive towards nucleophilic attack than the benzoyl group.[3b] (b) The fact that k_{CO} for *p*-nitrophenyl esters exceeds (by a factor of *ca.* 5) k_{CO} for the *ortho*-isomers in reactions with sodium benzenethiolate is in line with the expected leaving group ability of the corresponding phenols, as measured by their pK_a values.[17,18] A similar retarding *o*-nitro-group effect in the reactions of aryl acetates with different nucleophiles has been previously observed.[17,19] Movement of a nitro-group from a *para*- to an *ortho*-position has a higher decelerating effect in the dinitro-series than in the mononitro-one: in fact the k_{CO} value for 2,6-DNPB is *ca.* 45 times smaller than k_{CO} for 2,4-DNPB in contrast with the expected [20] leaving group ability of the corresponding phenols, as found in the acetate-catalysed hydrolysis of aryl acetates.[17] (c) Also for attack on the aromatic carbon a great (27-fold) decrease in reactivity is observed on going from 2,4-DNPB to 2,6-DNPB. This type of behaviour in nucleophilic displacement reactions has been already observed for the reactions of 1-chloro-2,4- and of 2-chloro-1,3-dinitrobenzene with sodium benzenethiolate in methanol,[21] a *ca.* 40-fold decrease in reactivity being observed on going from the former to the latter. (d) In contrast to attack on the carbonyl carbon, for attack on the dinitrophenyl carbon by benzenethiolate 2,4-DNPB is *ca.* 1.8 times more reactive than 2,4-DNPA, indicating a slightly better leaving group ability of benzoate than of acetate.

A study of the solvent effect on the rates and on the ratio of C_{CO}–O to C_{Ar}–O scission has also been performed for the reaction of two ester substrates, 2,4-DNPA and 2,4-DNPB, with sodium benzenethiolate. The results obtained with changing the solvent from ethanol to methanol are shown in Table 2. A comparison of the data at 22° reveals that for both esters k_{CO} and k_{Ar} are greater in ethanol than in methanol, *i.e.* the rate increases parallel the decreasing polarity of the medium. This effect is expected [22] for a reaction in which charge is more dispersed in the transition state than in the ground state. For k_{CO} similar behaviour has been observed by us [2] for the reaction of PNPA with sodium benzenethiolate: the process at 22° was about three-fold faster in ethanol than it was in methanol. The solvent effect on k_{Ar} is in line with that observed in the reaction of halogenonitrobenzenes with arenethiolates.[23]

Table 2 also shows that the percentage of attack at the carbonyl carbon decreases from *ca.* 24 to *ca.* 16% for 2,4-DNPB and from *ca.* 57 to *ca.* 48% for 2,4-DNPA on passing from methanol to ethanol. In other words, k_{Ar} increases somewhat more than k_{CO} with decreasing polarity of the medium. That the solvent effect is more pronounced for Ar than for CO attack is not surprising: charge would be less completely dispersed in the transition state for attack on the carbonyl group than in the transition state for substitution on aromatic carbon.[3b]

EXPERIMENTAL

Solvents.—Ethanol, methanol, and dioxan were purified as previously [2] reported and stored under nitrogen.

Materials.—The esters were prepared by acetylation and benzoylation of the corresponding phenols, using standard methods described in the literature.[24] Benzenethiol was purified by distillation under reduced pressure. *p*-Nitrophenol (PNP), *o*-nitrophenol (ONP), 2,4-DNP, 2,6-dinitrophenol (2,6-DNP), and 2,4,6-trinitrophenol (2,4,6-TNP)

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were recrystallized commercial specimens. 2,4-Dinitrophenyl phenyl sulphide, 2,6-dinitrophenyl phenyl sulphide, and phenyl 2,4,6-trinitrophenyl sulphide were prepared by condensation of the corresponding chloro-compounds with sodium benzenethiolate in ethanol [21,25] and recrystallized several times to constant m.p.

Apparatus.—Rate measurements were carried out with a Gilford 2400 S spectrophotometer. The Gilford was equipped with dual thermospacers through which water was circulated at 22 ± 0.1°. Temperatures were determined with a Gilford 2417-S temperature monitoring thermosensor.

Kinetics.—The spectrophotometric procedure previously described [2] was used. Dilute solutions of the esters were prepared in pure dioxan and kept frozen in the refrigerator when not used. All solutions of benzenethiol, prepared immediately prior to use, were made under nitrogen, the thiol being exposed to air for the minimum period; thiol concentration was determined by iodimetric titration. The buffer solution (thiol–thiolate) was prepared by mixing two thermostatted solutions of benzenethiol and of sodium ethoxide in ethanol. The concentration of thiolate anion was taken as equal to that of sodium ethoxide titrated with 0.01N-hydrochloric acid (Methyl Red–Bromocresol Green). The reactions were initiated by addition of 20 μl of the ester solution to a cuvette containing the buffer solution, which had been thermally equilibrated at the temperature of the experiments. The measurements were made against a blank cuvette containing all the constituents of the reaction mixture except the ester. The initial concentrations of ester were generally as follows: ONPA, ONPB, PNPA, and PNPB, 4×10^{-5}M; 2,4-DNPA and 2,4-DNPB, 10^{-5}M; 2,6-DNPB, 10^{-4}M. The range of benzenethiolate concentrations was 2×10^{-4}—0.5M; a large excess of free thiol over base ensured complete conversion of hydroxide and ethoxide ions into benzenethiolate.

In the case of the nitrophenyl esters *o*- or *p*-nitrophenolate release was generally followed at 418 or 400 nm, respectively. In the case of the dinitrophenyl esters the u.v. absorption due to the formation of both dinitrophenol and dinitrophenyl phenyl sulphide was followed at 341 for 2,4-DNPA and 2,4-DNPB and at 374 nm for 2,6-DNPB. In all cases the absorption of the substrate and of the other products of the reaction was negligible at the chosen wavelength.

Runs were set up so as to provide pseudo-first-order kinetics. In selected cases (Table 1) measurements were made at different concentrations of thiol, of base, and of both thiol and base. Linear plots of log $(\text{O.D.}_\infty - \text{O.D.}_t)$ against time were found to at least 90—95% reaction. The pseudo-first-order rate coefficients obtained were converted to second-order coefficients by dividing by the thiolate concentration.

The rate constants thus obtained are the overall rate constants for all reactions consuming substrate. In the case of the dinitrophenyl esters these rate constants include that for C_{CO}–O scission (k_{CO}) and that for C_{Ar}–O cleavage (k_{Ar}). The separation of the two rates was accomplished next. The second-order rate coefficient for the reaction forming dinitrophenol, k_{CO}, was calculated by multiplying the total second-order rate constant, k_{tot}, by the yield of dinitrophenol formed in the reaction. The rate constant k_{Ar} was then computed by subtracting k_{CO} from the overall rate constant k_{tot}. Each k value is the average of at least three independent values, the mean deviation being ±3%; the reproducibility of both k_{tot} and k_{CO} (and k_{Ar}) was satisfactory.

The effect of ionic strength on the rate constant and on the method of scission was investigated in runs with all the esters except ONPB and ONPA. Ionic strength was controlled by the addition of different amounts of lithium chloride in the buffers used for the determinations of both rate and percentage of C_{CO}–O scission: in the former case ionic strengths ranging from 0.000 2 to 0.5M were used, in the latter the range of ionic strength was 0.002—0.5M.

Reaction Products.—The fraction of bond scission was established by determining yields of the phenol formed in the reaction of the esters with sodium benzenethiolate. This we have done through both photometric (u.v.) measurements and product isolation experiments.

The photometric determination was accomplished by recording the change of optical density at suitable wavelengths, where phenol is the only absorbing species. From the ' mock ' infinite optical density and from the extinction coefficient of the phenol determined under the same conditions at the same wavelengths, it was thus possible to calculate the yield of phenol formed in the reaction.

Product analysis was performed as described below for the reaction of 2,4-DNPB with benzenethiolate. Similar procedures were used for all other esters.

Reaction of 2,4-DNPB *with Sodium Benzenethiolate in Ethanol.*—The general procedure involved reaction of 4×10^{-3} mol of the ester with an equivalent amount of the nucleophilic reagent in 95% ethanol. Sodium benzenethiolate was prepared by adding benzenethiol (in excess, to prevent solvolysis by free ethoxide and hydroxide ions) to a solution of sodium ethoxide in ethanol. At the end of the reaction dilute mineral acid was added and the mixture was evaporated with caution to dryness on the steam-bath at reduced pressure. The residue was taken up in ether and separated by extraction with dilute mineral base (10% KOH). The aqueous solution was acidified, some ether was added, and the two layers were separated. The ether layer was evaporated nearly to dryness and chromatographed on silica gel. The material eluted rapidly by ether was shown to be benzoic acid (0.38 g, 78%) from its m.p., not depressed on admixture with an authentic sample. A second crop (0.11 g, 15%) was shown to be 2,4-DNP from its m.p., not depressed on admixture with an authentic sample. No attempt was made to separate the ether layer from the first separation into components (2,4-dinitrophenyl phenyl sulphide and *S*-phenyl thiobenzoate). The two products were identified by t.l.c. analysis on silica gel (benzene).

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