An integrated nmr of compound I gave chemical shifts δ 1.10, 1.66, 2.20–2.80, 3.35, and 5.50, interpreted as 6, 2, 4, 0.4, and 0.6 protons, respectively.

2,4-Dinitrophenylhydrazones of Compounds 1 and 4.—Two grams each of compound 1 and 2,4-dinitrophenylhydrazine and 2 ml of concentrated hydrochloric acid were gently heated at 70–80° for 10 min in 70 ml of absolute ethanol. Compound **4** was treated in a similar manner. The cooled solutions wre filtered and the filtrates were discarded. The air-dried precipitates were extracted with two successive 50-ml portions of boiling ethanol. The precipitates were again dried in air. The melting points of the hydrazones **1A** and **4A** were 205–207° and 248–249°, respectively.

Anal. Calcd for $C_{24}H_{22}N_8O_9$ (**1A**): N, 19.10. Found: N, 19.23. Calcd for $C_{25}H_{16}N_8O_9$ (**4A**): N, 16.66. Found: N, 16.49.

Registry No.—1, 20452-84-0; **1A**, 20452-85-1; **2**, 20452-86-2; **3**, 20452-87-3; **4**, 20452-88-4; **4A**, 20452-89-5; **5**, 20452-90-8; **6**, 20452-91-9.

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Bond Fission in the Hydrolysis of 2,4-Dinitrophenyl Phosphate[1]

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The hydrolyses of 2,4- and 2,6-dinitrophenyl phosphate differ from those of most simple monophosphates in that the dianion, rather than the monoanion, is the most reactive species.[2,3]

It is assumed that the dianion generates phenoxide and metaphosphate ions, and the inorganic phosphate

$$ArO\,PO_3^{2-} \xrightarrow{\text{slow}} ArO^- + PO_3^- \xrightarrow[\text{fast}]{H_2{}^{18}O} H_2PO^{18}O_3^-$$

should therefore have 25% of the abundance of the water. Experiments in mixed aqueous organic solvents show that the phosphorus–oxygen bond is broken, as required by this mechanism. The aim of the present work was to confirm the phosphorus–oxygen bond fission for hydrolysis of the dianion in water, and in addition to determine the position of bond fission for hydrolysis at high pH, where part of the reaction involves attack of hydroxide ion upon the dianion.[3] (The over-all reaction rate is increased approximately sixfold by 1 *M* potassium hydroxide; however sodium and potassium chloride have marked salt effects on the spontaneous hydrolysis of the dianion, and, assuming that the potassium chloride and hydroxide exert similar salt effects, approximately half the reaction in 1 *M* hydroxide ion will involve attack of this reagent and the rest will be a salt-assisted spontaneous hydrolysis of the dianion.)

Inorganic phosphate was isolated after complete hydrolysis in ^{18}O-enriched water and its excess isotopic abundance, *N*, was determined. The results (Table I) show that hydrolysis of the dianion, at pH 6.0, introduces one oxygen of the water into inorganic phosphate, as expected.

Table I

Bond Fission in the Hydrolysis of 2,4-Dinitrophenyl Phosphate[a]

Reagent	N_{H_2O}[b]	N_P[b]	% N_P/N_{H_2O}
pH 6.0[c]	0.80	0.21	26
pH 6.0[c]	0.78	0.18	23
1 *M* KOH	1.37	0.31	23
1 *M* KOH	1.37	0.33	24
1 *M* KOH	0.73	0.19	26

[a] At 25.0° unless specified. [b] Atom per cent excess above normal. [c] At 45.0° with acetate buffer; the pH was readjusted during the reaction.

The dianion with alkoxide ion in methanol or ethanol gives both phenol and phenolic ether, showing that phosphorus- and aryl–oxy fission are occurring.[3] In water we find predominantly phosphorus–oxygen fission (Table I). The spontaneous hydrolysis of the dianion makes some contribution to the over-all reaction, even with 1 *M* hydroxide ion, but not enough to account for all the phosphorus–oxygen fission, and therefore the hydroxide ion is attacking the phosphorus atom, although attack upon the aryl group is important with alkoxide ion in alcohol.[3] For nucleophilic attack upon 2,4-dinitrophenyl tosylate it was found that the more polarizable reagents tended to attack the aryl group preferentially,[4] but amines have been shown to attack the phosphorus atom of 2,4-dinitrophenyl phosphate.[5] These changes in the site of attack with changes in reagent accord with Pearson's classification of "hard" and "soft" reagents.[6]

However there was some nucleophilic attack upon the aryl group in the reaction between the bis-2,4-dinitrophenyl phosphate monoanion and hydroxide ion.[7] In this system two aryl groups are available for attack, and the spontaneous hydrolysis makes little contribution to the over-all reaction in alkali. These results provide other examples of phosphorylation by anions of phosphate esters.[3,5,7] Phosphorylations of one anion by another have been considered as models for degradations of several biologically important phosphates.[8]

Experimental Section

Materials.—2,4-Dinitrophenyl phosphate was prepared and isolated as its cyclohexylamine salt, mp 145° (lit.[3] mp 147°). The water was distilled from $KMnO_4$ (twice) and its isotopic abundance was determined by equilibration with CO_2 which was analyzed mass spectrometrically.

Reaction Conditions.—The following conditions are typical. The aryl phosphate (1 g), as its cyclohexylamine salt, was dis-

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[1] (a) Abstracted from the thesis of J. M. Hellyer, submitted in partial fulfillment of the requirements of the Doctor of Philosophy degree of the University of California at Santa Barbara. (b) Support of this work by the National Institute of Arthritis and Metabolic Diseases of the U. S. Public Health Service is gratefully acknowledged.

[2] A. J. Kirby and A. G. Varvoglis, *J. Amer. Chem. Soc.*, **89**, 415 (1967).

[3] C. A. Bunton, E. J. Fendler, and J. H. Fendler, *ibid.*, **89**, 1221 (1967).

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[6] R. G. Pearson, *J. Amer. Chem. Soc.*, **85**, 3533 (1963).

[7] C. A. Bunton and S. J. Farber, *J. Org. Chem.*, **34**, 767 (1969).

[8] J. R. Cox and O. B. Ramsay, *Chem. Rev.*, **64**, 343 (1964); J. R. Cox and J. P. Cleveland, in the Symposium on Naturally Occurring Phosphate Esters, Newcastle, The Chemical Society, London, 1967; D. G. Oakenfull, D. I. Richardson, and D. A. Usher, *J. Amer. Chem. Soc.*, **89**, 5491 (1967).

solved in $H_2{}^{18}O$ (150 ml) and the solution was made alkaline and extracted with pentane to remove the cyclohexylamine. The pH of the solution was then adjusted and the hydrolysis was carried to completion. For reactions at pH 6 the dinitrophenol was extracted with chloroform; this step was omitted for reaction in alkali. Barium phosphate was then precipitated, redissolved in acid and reprecipitated, following procedures already described, and then converted into potassium dihydrogen phosphate using Dowex 50W-X8 resin in its acid form followed by neutralization with KOH. Potassium dihydrogen phosphate was then isolated following procedures already described,[9] and its ^{18}O abundance was determined by heating it *in vacuo* with phenylenediamine hydrochloride and guanidine hydrochloride and analyzing the evolved CO_2 mass spectrometrically.[10]

Registry No.—2,4-Dinitrophenyl phosphate, 2566-26-9.

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[10] C. A. Bunton and B. N. Hendy, *ibid.*, 627 (1963).

Base-Catalyzed Formation and Reactions of *o*-Nitrophenylacetamides[1a,b]

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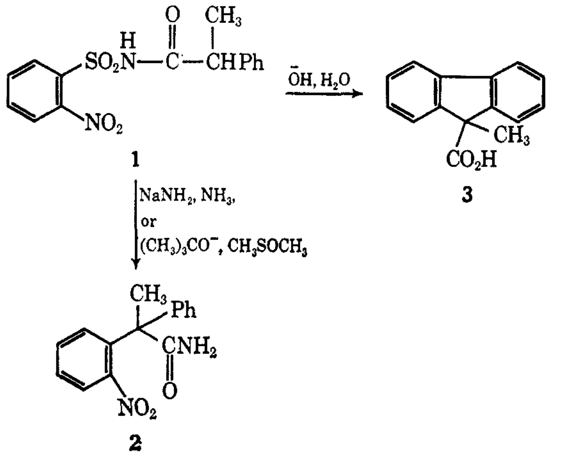
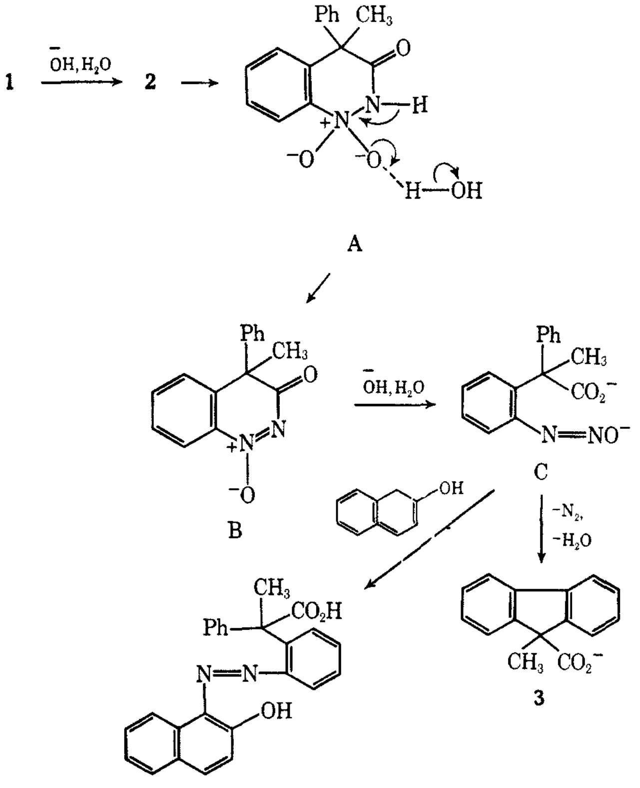
Naito and coworkers[2] have shown that Smiles rearrangement of N-(nitrophenylsulfonyl)acetamides can be a useful synthetic route to nitrophenylacetamides. We subjected N-(*o*-nitrophenylsulfonyl)-2-phenylpropionamide (**1**) to prolonged heating (26 hr) with 10% aqueous sodium hydroxide in an attempt to synthesize 2-(*o*-nitrophenyl)-2-phenylpropionamide (**2**) (Scheme I). The principal product of the reaction was found to be a nitrogen-free acid (30% yield). Spectral evidence and comparison with an authentic sample showed the acid to be 9-methylfluorene-9-carboxylic acid (**3**). It proved to be possible to synthesize **2** from **1** by using alternative basic catalysts. Sodium amide in liquid ammonia effects the transformation in 43% yield, whereas use of potassium *t*-butoxide in dimethyl sulfoxide gave **2** in 67% yield.

SCHEME I



We propose that the formation of **3** results from base-catalyzed intramolecular condensation of the amide and nitro groups in **2** and that the reaction follows the course outlined in Scheme II.

SCHEME II



The following observations can be cited in support of this proposal. When **2** is subjected to reaction with aqueous base, **3** is formed in 59% yield after 4.5 hr. Reaction of **1** with aqueous sodium hydroxide in the presence of *β*-naphthol leads to an azo compound believed to be **4** on the basis of analytical and spectral data. The formation of **4** suggests the intermediacy of a diazonium hydroxide (C) in the reaction. If C is formed by intramolecular condensation from **2**, the final step in the formation of 9-methylfluorene-9-carboxylic acid can readily be explained as a Pschorr cyclization.[3]

The intramolecular condensation between an amide group and nitro group which is proposed to account for the formation of intermediate B is an example of a relatively rare class of reactions, although condensations with many other types of carbon and nitrogen nucleophiles and nitro groups are quite common.[4] The formation of 3-phenylindazole when N-(*o*-nitrophenylsulfonyl)-2-phenylacetamide (**5**) is heated with aqueous base is believed to involve a similar condensation[2,4] proceeding *via* the Smiles rearrangement product **6** (Scheme III). An attempt was made to trap a di-

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[1] (a) Supported in part by NIH Grant GM-14344. (b) Abstracted from the Ph.D. Thesis of D. E. Blackburn, University of Virginia, 1969. (c) NASA Trainee, 1964–1967.

[2] T. Naito, R. Dohmori, and O. Nagase, *J. Pharm. Soc. Japan*, **74**, 593 (1954); T. Naito, R. Dohmori, and M. Sano, *ibid.*, **74**, 596 (1954); T. Naito, R. Dohmori, and M. Shimoda, *Pharm. Bull.* (Tokyo), **3**, 34 (1955).

[3] D. F. DeTar, *Org. Reactions*, **9**, 409 (1957).

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