

Experiment 3 was worked up as experiment 2. The phenylnitromethane, 4.46 g. (75%), had n_D^{20} 1.5315 to 1.5319, b.p. 91 to 93° (3 mm.). The residue from this distillation on recrystallization from 95% ethanol gave 0.08 g. (1%) of diphenylfuroxane (I), m.p. 114–115°, mixed m.p. with diphenylfuroxane undepressed.

Experiment 4 was worked up as in experiment 3. The recovered benzyl nitrite (0.9 g.) was yellow and had n_D^{20} 1.5006 to 1.5009; the phenylnitromethane (6.14 g.) had b.p. 99–102° (5 mm.), n_D^{20} 1.5312 to 1.5315. The diphenylfuroxane (1.22 g., 15% yield) had m.p. 115–116°.

Experiment 5.—On working up as in experiment 3, 5.29 g. (66% recovery) of benzyl nitrite was isolated, b.p. 45 to 52° (5 mm.), n_D^{20} 1.5008 to 1.5011. No phenylnitromethane was detected. The diphenylfuroxane, 7.21 g. (82% yield), had m.p. 114–115°, mixed m.p. undepressed.

Preparation of Phenylnitrolic Acid.—The procedure of Wieland and Semper⁷ was used three times. Crystalline products were obtained which decomposed spontaneously at room temp. as soon as they were isolated, large volumes of brown gases being produced. Two further experiments in which the procedure was modified by using nitrosyl chloride in place of nitrous acid failed to give any of the desired product. Phenylnitrolic acid was finally obtained as follows: sodium, 0.69 g. (0.03 mole) was dissolved in 100 ml. of dry methanol and then 4.11 g. (0.03 mole) of phenylnitromethane in 15 ml. of methanol was added at room temperature. The methanol was promptly removed *in vacuo*; the resulting salt was an ivory-white powder. Anhydrous ether, 100 ml., was then added, the mixture was stirred and the finely divided slurry was cooled to –78°. Dinitrogen trioxide (b.p. 10 to 13°) was vaporized through a tube packed with phosphorus pentoxide on glass beads, recondensed, and then allowed to drip into the well-stirred slurry. The addition was continued until a green-blue color persisted (*ca.* 2 hours). The reaction mixture was then stored overnight at –80°, washed with ice-water, and then extracted with small portions of ice-cold 2% aqueous ammonia retaining only those extracts colored orange-red. The combined orange-red extracts were layered with ice-cold ether and acidified (disappearance of orange-red color) with ice-cold saturated oxalic acid solution; the acidified solution was extracted two more times with cold ether. The ether extracts were washed with ice-water and dried over magnesium sulfate at –80°. The ether was removed *in vacuo* at, or below, 0°; pale yellow, crystalline phenylnitrolic acid, m.p. 55–57° dec., lit.⁷ 57–58° dec., was obtained; 2.15 g. (48% yield); neut. equiv. calcd. for $C_7H_5N_2O_3$, 166; found (potentiometrically), 163.

Decomposition of Phenylnitrolic Acid. (a) At 25°.—Phenylnitrolic acid (1.0 g., 0.006 mole) was dissolved in a solution of 10 ml. of DMF containing 0.88 g. of urea and 0.63 g. (0.009 mole) of sodium nitrite. Within 15 seconds a colorless gas began to be evolved. The reaction flask was kept in a 25° bath for 14 hours after which the solution was poured into ice-water and extracted with ether. The combined extracts were washed with 5% aqueous sodium bicarbonate. The bicarbonate extracts were then acidified with hydrochloric acid and extracted with ether. The ether extracts were washed with water and dried over magnesium sulfate. When the ether was removed *in vacuo* 0.59 g. (81% yield) of benzoic acid, m.p. 119–121°, mixed m.p. 119–121°, was obtained.

The initial ether extracts, which had been washed with sodium bicarbonate solution, were washed with water and dried over magnesium sulfate. When the ether was removed *in vacuo* 0.02 g. (*ca.* 3%) of diphenylfuroxane (yellow crystals) was isolated, m.p. 109–113°.

(b) At –16 to –18°.—A duplicate experiment was conducted at –16 to –18° for 19 hours. The yield of benzoic acid was 0.06 g. (8%), m.p. 119–121° and that of diphenylfuroxane (I) was 0.56 g., m.p. 111–114°; recrystallization from ethanol gave 0.53 g. (74% yield), m.p. 114–115°.

Reaction of *p*-Nitrobenzyl Bromide with Sodium Nitrite in DMF.—Five experiments at temperatures of –16°, –10° and 25° were run; the reaction times ranged from 15 min. to 24 hours. The run at –16° for 15 minutes gave a 22% yield of *p*-nitrophenylnitromethane, yellow crystals, m.p. 88–91°, lit.¹⁷ m.p. 90–91°. Substantial amounts of other products (not characterized) were obtained. Another run at –10° for 50 minutes gave, in addition to a 7% recovery of *p*-nitrobenzyl bromide, a 2% yield of *p*-nitrophenylnitromethane, a 31% yield of bis-*p*-nitrophenylfuroxane, m.p. 199–201°, lit.¹⁸ m.p. 197–198°; a Nujol mull had the characteristic furoxane bands.¹⁸ In addition, a 4% yield of the acetal of *p*-nitrobenzaldehyde with *p*-nitrobenzyl alcohol¹¹ was isolated, m.p. 209–211°; an authentic sample¹¹ melts at 210–211°; finally, a mixture of *p*-nitrobenzaldehyde and *p*-nitrobenzyl alcohol (in unknown proportions) was converted to *p*-nitrobenzoic acid by alkaline permanganate; yield 10%, m.p. 239–240°; a mixed m.p. with authentic *p*-nitrobenzoic acid was undepressed.

(17) N. Kornblum, R. A. Smiley, R. K. Blackwood and D. C. Ifland, *THIS JOURNAL*, **77**, 6269 (1955).

(18) A. Werner, *Ber.*, **27**, 2848 (1894).

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[CONTRIBUTION FROM THE VENABLE CHEMICAL LABORATORY, UNIVERSITY OF NORTH CAROLINA]

The Nucleophilic Reactivity of Aniline, Hydrazine and Phenoxide Ion toward 2,4-Dinitrochlorobenzene¹

BY J. F. BUNNETT AND GEORGE T. DAVIS

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With 2,4-dinitrochlorobenzene in 60% dioxane, aniline reacts considerably slower and hydrazine somewhat faster than hydroxide ion (see Table I). Addition of excess phenol causes the rate coefficient for the phenoxide reaction at first to rise and then to fall (Fig. 1); this effect is briefly discussed.

In an earlier paper² we reported rates of reactions of several nucleophilic reagents with 2,4-dinitrochlorobenzene in 60% dioxane solution. We now add similar data for the reagents aniline and hydrazine. The effect of phenol, in various concentrations, on the rate of reaction of phenoxide ion with this substrate is also reported.

Earlier work³ has shown that hydrazine is a mod-

erately strong nucleophilic reagent toward 2,4-dinitrochlorobenzene, whereas aniline is rather weak amongst amines in this regard. However, results obtained hitherto have not served to establish quantitatively, under uniform conditions, the nucleophilic reactivity of these reagents in respect to other reagents of diverse character.

Rate coefficients determined in the present work for aniline and hydrazine reactions are set forth in

(1) Research supported by the Office of Ordnance Research, U. S. Army.

(2) J. F. Bunnett and G. T. Davis, *THIS JOURNAL*, **76**, 3011 (1954).

(3) H. J. van Opstall, *Rec. trav. chim.*, **52**, 901 (1933); F. L. J. Sixma, *ibid.*, **74**, 168 (1955); A. Singh and D. H. Peacock, *J. Phys.*

Chem., **40**, 669 (1936); S. D. Ross and I. Kuntz, *THIS JOURNAL*, **76**, 3000 (1954); J. J. Blanksma and H. H. Schreinemachers, *Rec. trav. chim.*, **52**, 428 (1933).

Table I. Runs were designed to facilitate observation of second-order kinetics, and good second-order kinetics were observed throughout. In most runs the progress of the reaction was followed by photometric measurements. In two aniline runs samples were titrated for chloride ion, and the rate coefficients from these runs agreed well with those determined photometrically.

TABLE I
REACTIONS WITH 2,4-DINITROCHLOROBENZENE IN 60% DIOXANE

Reagent	Temp., °C.	[ArCl] ₀	[Reagent]	Rate coefficient, l. mole ⁻¹ sec. ⁻¹ × 10 ³
Hydrazine	25.32	0.0302	0.0335	4.00
		.0348	.0334	3.87
		.0341	.0334	3.87
	45.90	.0347	.0336	17.4
		.0363	.0340	17.5
Aniline	25.32	.0150	.0301	0.0837
		.0150	.0301	.0775
		.0151	.0302	.0820 ^a
		.0149	.0298	.0766 ^a
		.0149	.0298	.0829
		.0178	.1502	.0845
	25.20	.0147	.1502	.0860
	45.90	.0147	.0298	.305
		.0147	.0298	.302

^a Reaction followed by titration of chloride ion.

Rate coefficients at 25.2°, plus energies and entropies of activation for reactions of six reagents with 2,4-dinitrochlorobenzene are displayed in Table II; this table combines results from the present and the earlier² study. Methoxide ion, which was included in the corresponding table in the earlier paper, is now omitted because the indirect method used to evaluate its rate coefficient is of dubious validity.⁴

TABLE II
REACTIONS OF 2,4-DINITROCHLOROBENZENE WITH NUCLEOPHILIC REAGENTS IN 60% DIOXANE

Reagent	Rate coefficient at 25.2°, l. mole ⁻¹ sec. ⁻¹	ΔE‡, kcal./mole	ΔS‡, cal./deg.
C ₆ H ₅ NH ₂	0.0799 × 10 ⁻³	12.2	-38.4
OH ⁻	1.10 × 10 ⁻³	17.5	-15.4
N ₃ H ₄	3.87 × 10 ⁻³	13.8	-25.4
C ₆ H ₅ O ⁻	12.7 × 10 ⁻³	14.7	-20.2
Piperidine	74.6 × 10 ⁻³	10.5	-30.5
C ₆ H ₅ S ⁻	(22000 × 10 ⁻³) ^a		

^a Value estimated indirectly; see ref. 2.

It will be noted that hydrazine⁵ shows nucleophilic reactivity intermediate between hydroxide ion and phenoxide ion whereas aniline is considerably weaker as a nucleophilic reagent. It is interesting that the aniline reaction has a considerably lower energy of activation than the hydrazine reaction; hydrazine's superior over-all reactivity derives from a larger (less negative) entropy of activation. This favorable entropy term may be a consequence of hydrogen bonding between β-hydrogens of hydrazine and oxygen of the 2-nitro group; such interaction would be expected to reduce the re-

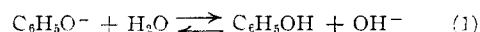
(4) Cf. B. D. England, *Chemistry & Industry*, 1145 (1954).

(5) Division of the hydrazine rate coefficient by a statistical factor of two gives the rate coefficient per amino group.

quirement of the transition state for solvation, and thus increase the entropy of activation.⁶

Ross and Kuntz³ observed that the aniline rate coefficient for reaction in ethanol or in 50% ethanol-50% ethyl acetate decreased as the concentration of aniline increased. The disturbance was ascribed to charge-transfer complex formation. To see whether this factor was affecting our rate measurements, we did two runs (Table I) with aniline concentration 0.15 *M*, this being five times the usual concentration. The rate coefficients for these runs were nearly the same as at the usual aniline concentration. It is thus shown that Ross and Kuntz' factor does not affect reactivity under the conditions of our experiments.

It was recognized in the earlier paper² that the reported rate coefficient for reaction of phenoxide ion with 2,4-dinitrochlorobenzene might be low by about 9% owing to destruction of some phenoxide by the reaction



This reaction produces hydroxide ion, a weaker nucleophilic reagent. Disturbances of similar origin have been noted^{4,7} in reactions involving phenoxide ion in alcoholic solvents, although in such cases a falsely *high* rate coefficient is observed because common alkoxides have greater nucleophilic reactivity than phenoxide ion. The disturbance, if it is not too serious,⁴ can be suppressed by addition of excess phenol⁷ which forces equilibrium 1 to the left.

We therefore determined the effect of added excess phenol on the rate of the phenoxide reaction. Data are listed in Table III and summarized in Fig. 1. It will be noted that addition of phenol causes the rate to increase slightly, as expected, up to a phenol:phenoxide ratio of about 3:1 (moles phenol:moles NaOH ratio of 4:1) but that additional phenol causes the rate to *decrease*. All the effects are small, the maximum variation in rate in Table III being only 14%, but they were reproducible. In this connection it should be noted that the runs in Table III are listed in their chronological order of performance; the fact that runs at any concentration of phenol were reproducible independent of their order of performance shows that the effects observed are not merely the consequence of a time-variable systematic error.

The initial rise in the curve in Fig. 1 is ascribed to suppression of reaction 1 as discussed above. The later drop was unexpected. A tentative explanation for the drop is that excess phenol may combine to some extent with phenoxide ions to form biphenoxide ions, C₆H₅OH·OC₆H₅⁻, of lower nucleophilic reactivity. This is an interesting effect, and it warrants further study.

The rate coefficient at the maximum in Fig. 1, 1.27 × 10⁻² l. mole⁻¹ sec.⁻¹, is perhaps best representative of the reactivity of phenoxide ion with 2,4-dinitrochlorobenzene. This is the value listed in Table II.

Experimental

Materials.—2,4-Dinitrochlorobenzene, phenol and 60%

(6) Cf. J. F. Bunnett and R. J. Morath, *THIS JOURNAL*, **77**, 5051 (1955).

(7) J. W. Baker and A. J. Neale, *Nature*, **172**, 583 (1953); *J. Chem. Soc.*, 3225 (1954).

TABLE III
REACTION OF SODIUM PHENOXIDE WITH 2,4-DINITROCHLORO-
BENZENE IN 60% DIOXANE AT 25.20°

[ArCl] ₀ , mole/l.	NaOH used, mole/l.	Phenol used, mole/l.	Moles phenol Mole NaOH	Rate Coeffi- cient, ^a 1. mole ⁻¹ sec. ⁻¹ × 10 ³
0.0149	0.0299	0.0299	1.00	11.75
.0151	.0302	.0302	1.00	11.58
.0151	.0302	.0608	2.01	11.95
.0151	.0151	.0670	4.44	12.38
.0151	.0151	.0712	4.71	12.07
.0151	.0151	.1212	8.02	11.12
.0152	.0152	.1206	7.96	11.18
.0154	.0154	.1207	7.81	11.12
.0151	.0151	.0151	1.00	11.58
.0152	.0152	.0304	2.00	12.23
.0151	.0151	.0469	3.11	11.92
.0152	.0152	.0765	5.04	11.67
.0152	.0152	.0605	3.97	12.72
.0152	.0152	.0718	4.74	12.40

^a Runs are listed in the chronological order in which they were performed.

aqueous dioxane were prepared as previously described.² Aniline was redistilled and stored under nitrogen. 2,4-Dinitrodiphenylamine, m.p. 157–157.5° (lit.³ 156–156.4°), was prepared from aniline and 2,4-dinitrochlorobenzene and was recrystallized twice from absolute ethanol. Commercial 2,4-dinitrophenylhydrazine was recrystallized.

Apparatus.—Thermostats were constant to ±0.02°, and thermometers were checked against National Bureau of Standards-certified thermometers. Pipets were calibrated. Photometric measurements were made with a Beckman model B spectrophotometer.

Rate Measurements.—All runs with phenoxide ion and two runs with aniline were followed by titration of chloride ion according to the procedure previously described.² Most of the aniline runs and all the hydrazine runs were followed by photometric measurements,⁹ made at 400 or 410

(9) J. F. Bunnett and H. D. Crockford, *J. Chem. Education*, **33**, 552 (1956).

(8) T. L. Davis and A. A. Ashdown, *THIS JOURNAL*, **46**, 1052 (1924).

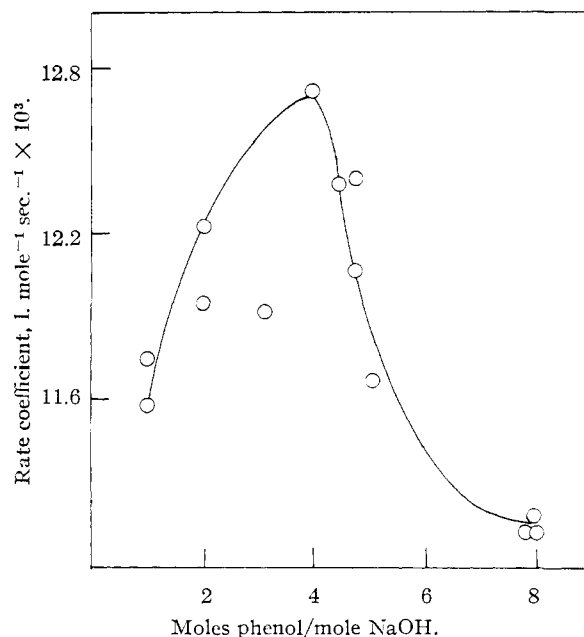


Fig. 1.—Rate of reaction of phenoxide ion with 2,4-dinitrochlorobenzene as affected by phenol concentration.

mμ for aniline runs and at 450 mμ for hydrazine runs. Some difficulty was experienced with deterioration of hydrazine standard solutions. Eventually, a procedure was developed whereby a stock solution of hydrazine of approximately the desired concentration was prepared and aliquots were withdrawn as nearly simultaneously as possible (a) for combination with 2,4-dinitrochlorobenzene in 60% dioxane to start a kinetic run and (b) for addition to excess aqueous acid in preparation for titration against standard potassium iodate solution.¹⁰ Rate coefficients and energies and entropies of activation were calculated by appropriate standard expressions.

(10) R. A. Penneman and L. F. Audrieth, *Anal. Chem.*, **20**, 1058 (1948).

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Structure of 2,6,6-Trimethyl-2,4-cyclohexadienone Dimer¹

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The lithium salt of 2,6-dimethylphenol has been found to react with methyl iodide (in the absence of any other solvent) to form, in addition to 38% of the expected methyl ether III, 22% of 2,6,6-trimethyl-2,4-cyclohexadienone (I). The dienone readily forms a dimer (II) which is now shown by an examination of the infrared and ultraviolet spectra and the dipole moment of 1.71 D. measured in cyclohexane to have the structure A. The dienone, after dimerization, readily can be separated by distillation of the ether III under reduced pressure. The dienone can then be recovered from the dimer (which may be purified by recrystallization) by distillation at higher temperatures. The method thus is a practical one for the synthesis of such dienones.

In the course of a study of the formation of cyclohexadienones by the direct *o*-alkylation of phenol salts with organic halides² it has been found that 2,6,6-trimethyl-2,4-cyclohexadienone (I) is readily prepared by the reaction of lithium 2,6-

(1) Supported in part by the Office of Ordnance Research, U. S. Army.

(2) (a) D. Y. Curtin and R. J. Crawford, *Chemistry & Industry*, 313 (1956); (b) *THIS JOURNAL*, **79**, 3156 (1957); (c) D. Y. Curtin and R. R. Fraser, *Chemistry & Industry*, 1358 (1957); (d) D. Y. Curtin, R. Crawford and M. Wilhelm, *THIS JOURNAL*, **80**, 1391 (1958); (e) D. Y. Curtin and M. Wilhelm, *J. Org. Chem.*, **23**, 9 (1958).

