the N-phenyl and N-*p*-tolyl homologs, respectively. These values may be interpreted as indicating that the primary effect of the substituents is on the acidity of the bromoamide.

Experimental

N-Phenyl-4-bromobutanamide.—Twenty ml. of thionyl chloride was added dropwise to 37.1 g. of 4-bromobutanoic acid and the mixture was allowed to remain at room temperature for two days. The excess thionyl chloride was removed by means of a water aspirator and the residue vacuum distilled, b.p. 88–90° at 31 mm., $n^{25}\text{D}$ 1.4899. A solution of 37.2 g. of aniline (0.4 mole) in 500 ml. of chloroform was treated dropwise with stirring with 37.1 g. of this distillate. After addition of the acid chloride the solution was stirred an additional 15 minutes. The precipitate of aniline hydrochloride was removed and washed with three 20-ml. portions of chloroform. The chloroform filtrate and washings were concentrated by means of a water aspirator and the crude bromobutanamide was purified by dissolving in hot petroleum ether (b.p. 65–110°), cooling and then chilling the solution in a Dry Ice–acetone solution. The recrystallized product melted at 75–76°. The yield based on recrystallized product was 38%.

Anal. Calcd. for $C_{10}H_{12}ONBr$: Br, 33.00. Found: Br, 32.97.

N-*p*-Tolyl-4-bromobutanamide.—This compound was prepared in an analogous manner as N-phenyl-4-bromobutanamide except that the reaction time was extended to two hours. A yield of 63.2% of recrystallized bromoamide (pet. ether) was obtained; m.p. 90–91°.

Anal. Calcd. for $C_{11}H_{14}ONBr$: Br, 31.20. Found: Br, 31.20.

N-*p*-Chlorophenyl-4-bromobutanamide.—By employing the procedure described above and a reaction time of two hours, a 69.2% yield of bromoamide was obtained. Recrystallization was from pet. ether, m.p. 100–101°.

Anal. Calcd. for $C_{10}H_{11}ONClBr$: Br, 28.88. Found: Br, 28.88.

1-*p*-Chlorophenylpyrrolidone.—One hundred ml. of a methanol solution 0.05 *M* with respect to sodium methoxide and 0.05 *M* with respect to N-*p*-chlorophenyl 4-bromobutanamide was placed in a water-bath at 22.9° until all the bromide ion was released. The methanol was evaporated off by means of a water aspirator and the residue washed with water to remove the sodium bromide. The residue was dried in an oven at 50° and weighed 0.940 g. (96%) and melted from 84–92°. The crude 1-*p*-chlorophenylpyrrolidone was recrystallized from low boiling petroleum ether (30–60°) and melted from 95–97°.

Anal. Calcd. for $C_{10}H_{10}ONCl$: N, 7.16. Found: N, 7.38.

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NOTES

The Reactivity of the Chloronitrobenzenes with Sodium Thiophenoxide

BY J. F. BUNNETT AND R. F. SNIPES

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It has long been known[1] that halogen atoms are displaced readily from *o*- and *p*-halonitrobenzenes by mercaptide reagents, nitrophenyl sulfides being formed, whereas *m*-halonitrobenzenes do not undergo this sort of reaction. Little is known, however, about the reactivity of *o*- as compared to *p*-halonitrobenzenes in such reactions.

Bourgeois and Huber[1] reported that *o*-bromonitrobenzene reacted with sodium thiophenoxide in absolute ethanol more energetically than its *para* isomer did. From this, Bunnett and Zahler[2] surmised that *o*-halonitrobenzenes exceed their *para* isomers in reactivity toward this reagent. The present experiments, undertaken in connection with other work on the *ortho:para* ratio in activation of aromatic nucleophilic substitution by the nitro group,[3] indicate that this surmise was incorrect.

We have measured rate coefficients for the reactions of *p*-chloronitrobenzene (I), of *o*-chloronitrobenzene (II) and of 1,4-dichloro-2-nitrobenzene (III) with sodium thiophenoxide in 60% dioxane solution at 25.35°. Rates were followed spectrophotometrically, and in a few cases by potentiometric titration of the chloride ion liberated. Results are listed in Table I.

TABLE I

REACTIONS WITH SODIUM THIOPHENOXIDE IN 60% DIOXANE

Substrate, nitrobenzene	Rate coefficient at 25.35°, l. mole^{-1} min.$^{-1}$			
	Photometric		By titration	
	Indiv. runs	Mean	Indiv. runs	Mean
p-Chloro- (I)	0.0295			
	.0307			
	.0282[a]	0.0295	0.0252[a]	
o-Chloro- (II)	.0047			
	.0043			
	.0058			
	.0038	.0046		
1,4-Dichloro-2- (III)	.216		.200	
	.218	.217	.194[b]	
			.179[b,c]	
			.165[b,c]	0.184

[a] These two coefficients are derived from analysis of portions of the same reacting mixture. [b] These coefficients are 101% of coefficients measured at 25.25°. [c] From reference 4.

That the reactions are not entirely free of complications is indicated by the difference between the photometric and titrimetric rate coefficients, by the variation of rate coefficients from run to run (especially in reactions of II), and by the fact that infinity optical densities for runs with III were only 87% of theoretical. On the other hand, the approximate agreement of rate coefficients measured by the two techniques, the spectra of reaction

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(1) E. Bourgeois and P. Huber, *Bull. soc. chim.*, [4] **9**, 944 (1911).

(2) J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 312 (1951).

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

solutions from all three compounds, and the isolation of the expected product from III[4] indicate that the coefficients measured represent for the most part the expected displacement of chlorine by the thiophenoxy group.

The data show that *p*-chloronitrobenzene reacts with sodium thiophenoxide, under the conditions of our experiments, 6.4 times as fast as *o*-chloronitrobenzene. The *para* isomer is known to react more rapidly, by about the same margin, with alkoxide reagents.[2] We tentatively conclude that the chlorine atom in *p*-chloronitrobenzene in general is replaced more readily by anion reagents.[5]

The data in Table I for the last two substrates permit a recalculation[4] of the Hammett ρ-constant for the reactions of 4-substituted-2-nitrochlorobenzenes with sodium thiophenoxide in 60% dioxane. The three points now available (for H, *p*-Cl and *p*-CF_3) fall neither precisely in line nor so far out of line as to raise doubt about the applicability of the Hammett treatment. Rho, calculated by the method of least squares, is +4.5. This is somewhat higher than previously estimated, but still of the same order of magnitude as ρ-constants for other nucleophilic displacements at aromatic carbon atoms.[6]

Experimental

Materials.—I, II and III were commercial products recrystallized. *o*-Nitrodiphenyl sulfide, m.p. 80°, *p*-nitrodiphenyl sulfide, m.p. 54–55°, and 4-chloro-2-nitrodiphenyl sulfide, m.p. 84–85.5°, were prepared, for use in standardizing the spectrophotometric analytical method, by condensation of the corresponding chloro compounds with sodium thiophenoxide in alcoholic or aqueous dioxane media. 60% Dioxane (by volume) was prepared as previously described.[4] Commercial thiophenol was redistilled and stored in a nitrogen atmosphere. Standard solutions of sodium thiophenoxide in 60% dioxane were prepared by combining weighed amounts of thiophenol with calculated volumes of standard sodium hydroxide. These solutions contained about 0.02 mole of sodium hydroxide per 0.15 mole of sodium thiophenoxide, to ensure complete conversion of thiophenol to thiophenoxide ion, and were used within one day of their date of preparation. The presence of free hydroxide ion can be tolerated because hydroxide ion is such a poor nucleophilic reagent compared to thiophenoxide ion.[4]

Rate Measurements.—In the reaction solutions, the concentrations of sodium thiophenoxide and the aryl chloride were equal and about 0.015 *M*. At measured times, samples were quenched by excess sulfuric acid and analyzed by titration[4] or by spectrophotometric measurements[3] as previously described. Reactions were followed to about 50, 30 and 50% of completion, respectively, in the cases of substrates I, II and III. Plots $1/(a - x)$ *vs.* t were strictly linear in the case of I, whereas the rate coefficient decreased slightly (less than 10% from beginning to end) in the case of III, and decreased in a more pronounced fashion (20% in the extreme) in the case of II.

Reactions of all three aryl chlorides were allowed to stand for several days after the completion of kinetics runs, and then samples were removed and diluted in a standard fashion. At the same time, samples were removed from synthetic infinity solutions made from the pure sulfide products, and these samples were diluted in the same fashion. The visible and ultraviolet absorption spectra of the corresponding diluted samples were determined and compared one against the other. The spectra showed that I, II and III had formed, respectively, 69, 42 and 87% of the expected sulfides. The last was a maximum value which did not increase with time. In all three cases, the spectra of the reaction solutions closely resembled the spectra of the pure products, indicating that the expected products had been formed.

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

[5] *o*-Chloronitrobenzene is more reactive toward amines.[2]

[6] J. F. Bunnett, H. Moe and D. Knutson, THIS JOURNAL, **76**, 3936 (1954); E. Berliner and L. C. Monack, *ibid.*, **74**, 1574 (1952).

Many-membered Carbon Rings. XI.[1] Civetone Homologs

BY A. T. BLOMQUIST AND JOSEPH WOLINSKY

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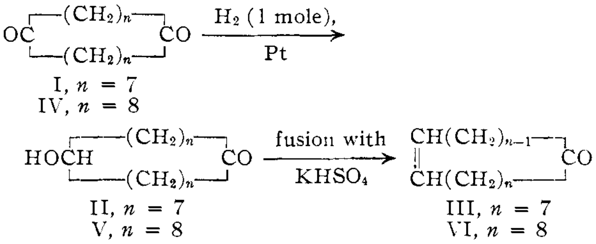
Although several syntheses for the perfumery fixative civetone have been developed,[2] little attention has been given to the synthesis of civetone homologs possessing the important musk odor. Ruzicka's method for 8-cyclohexadecen-1-one (III) and 9-cyclooctadecen-1-one (VI)[3,4] *via* the pyrolysis of the appropriate dibasic acids is not particularly attractive as the yields of ketones are quite low and the syntheses of the requisite unsaturated dibasic acids are lengthy.

The successful use of 1,9-cyclohexadecanedione (I) and 1,10-cyclooctadecanedione (IV) as precursors for muscone analogs[1] prompted a study of the utility of I and IV as intermediates for the synthesis of III and VI. The latter were in fact easily obtained by dehydration of the hydroxyketones II and V, prepared by the partial reduction of I and IV.



Using Adams catalyst in acetic acid, partial reduction of I was achieved by allowing one equivalent of hydrogen to be absorbed. The resulting mixture of products then was recrystallized from hexane, 1,9-cyclohexadecanediol (VII) being insoluble at room temperature and nearly pure II separating on cooling to 0–5°. Unreduced I and II, contained in the mother liquor, were separated by chromatography. II, thus obtained in 60% yield and characterized as its semicarbazone derivative, on fusion with potassium hydrogen sulfate gave III, isolated as its semicarbazone derivative (80%). Oxalic acid hydrolysis of III semicarbazone gave pure III, m.p. 17–22°, having an intense musk odor.

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[1] For the preceding paper in this series see A. T. Blomquist, J. Prager and J. Wolinsky, THIS JOURNAL, **77**, 1804 (1955).

[2] E. H. Rodd, "Chemistry of Carbon Compounds," Elsevier Publishing Co., New York, N. Y., 1953, Vol. II, Part A, p. 277.

[3] L. Ruzicka, M. Stoll, W. Scherrer, H. Schinz and C. F. Seidel, *Helv. Chim. Acta*, **15**, 1459 (1932).

[4] Soc. anon. M. Naef and Cie, Swiss Patent 135,921 (1928); *C. A.*, **24**, 2761 (1930); L. Ruzicka, U. S. Patent 1,873,154; *C. A.*, **26**, 5965 (1932).