tration and cooling, filtration, etc., until no more precipitate formed yielded 4.51 g. of crude white needles, m.p. 173–180°. A sample recrystallized from ethanol melted at 184–184.8° dec. The compound's infrared spectrum was blank between 1500 and 2800 cm.$^{-1}$ and showed no hydroxyl absorption.

Anal. Found: C, 40.88; H, 4.44; Cl, 50.67.

No further work was done on the solid product.

Fractionation of the crude mother liquors yielded 11.62 g. (12%) of pure 2,2-dichlorocyclohexanone.

2-Chlorocyclohexenone.—Cyclohexenone was converted to 2-chlorocyclohexenone according to the directions of Richter and Kotz.[9] Infrared absorption occurred at 1705, 1675 (shoulder), 1657 (w) and 1617 cm.$^{-1}$.

Anal. Calcd. for C_6H_7OCl: C, 55.18; H, 5.40; Cl, 27.15. Found: C, 55.15; H, 5.31; Cl, 26.88.

3-Chlorocyclohexane-1,2-dione.—To a solution of 727 mg. (0.0039 mole) of cyclohexanone-2,6-dicarboxylic acid[8] in 5 ml. of water was added a solution of *ca.* 20 molar equivalents of chlorine in carbon tetrachloride. After allowing the solution to stand for a few minutes with frequent shaking, excess chlorine was removed by subjecting the solution to a water-pump vacuum, the solution was made alkaline with a saturated solution of potassium bicarbonate and warmed to 60–65° for 15 minutes, the aqueous layer turning yellow in the process.

After cooling, the layers were separated and the aqueous layer extracted with four 50-ml. portions of ether. The combined organic layers were dried over magnesium sulfate and concentrated in vacuum to a brownish solid weighing 399 mg. Sublimation at 55° (0.02 mm.) yielded 157 mg. of square white plates contaminated with a colorless oil.

Recrystallization from ether-*n*-pentane at 0° gave 143 mg. (25%) of square plates, m.p. 119–122°. Repeated sublimation and recrystallization from low-boiling petroleum ether at 0° raised the melting point to 120.2–122°. The compound gave a strong violet color with ferric chloride, dissolved readily in 10% potassium carbonate solution, and gave a positive Beilstein test. Infrared absorption occurred at 3450, 1685 and 1656 cm.$^{-1}$.

Anal. Calcd. for $C_6H_7O_2Cl$: C, 49.17; H, 4.81; Cl, 24.19. Found: C, 49.14; H, 5.02; Cl, 24.05.

This material is different from Reimschneider's[10] Δ^3-3-chlorocyclohexen-1,2-dione which manifested infrared absorption at 3470, 1770 and 1725 cm.$^{-1}$.

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[9] A. Kotz and K. Richter, *J. prakt. Chem.*, **111**, 373 (1925).

[10] R. Reimschneider, *Monatsh.*, **85**, 417 (1954).

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BUCKNELL UNIVERSITY]

On Cyclic Intermediates in Substitution Reactions. VII. The Alkaline Solvolysis of Some N-Aryl-4-bromobutanamides

BY HAROLD W. HEINE, PETER LOVE AND JOHN L. BOVE

RECEIVED MAY 21, 1955

The rates of alkaline solvolysis of three N-aryl-4-bromobutanamides have been studied in methanol. The rates of reaction as determined by the measurement of the release of bromide ion are of the first order with respect to bromoamide and first order with respect to methoxide ion. The reaction products are the corresponding pyrrolidones. These results are discussed in terms of a mechanism involving the formation and conversion of a bromoamido ion to a pyrrolidone. The syntheses of three new bromoamides and one new pyrrolidone are described.

Earlier papers of this series[1] examined quantitatively the ease of participation of neighboring groups in internal displacement reactions in systems where the distance between the carbon atom on which displacement occurs and the participating neighboring group is increased.

The present investigation concerns itself with the alkaline solvolysis of some N-aryl-4-bromobutanamides. The products obtained in high yields from the solvolytic reactions were the corresponding N-arylpyrrolidones. Since 1-*p*-tolylpyrrolidone and 1-phenylpyrrolidone have previously been characterized[2,3] only the isolation of 1-*p*-chlorophenylpyrrolidone is described in detail in the Experimental section. The kinetics of the reaction, as followed by measurement of released bromide ion as a function of time, was found to be first order with respect to methoxide ion and first order with respect to bromoamide. The N-aryl-4-bromobutanamides studied were so chosen as to provide a test of the basis for a mechanism which involved a rapid reversible proton transfer from amide to methoxide ion followed by an internal displacement of bromide by the formed amido ion.

Method of Rate Measurement.—The measurements were carried out in a water-bath in which the temperature was thermostatically controlled to ±0.02°. A quantity of bromoamide sufficient to make the concentration lie within the range of 0.04–0.05 *M* was introduced into a 100-ml. volumetric flask which contained a known quantity of preheated standardized sodium methoxide solution sufficient to make the final concentration of methoxide 0.04–0.19. Anhydrous methanol preheated to bath temperature was then quickly added to the mark, the solution was shaken, and at convenient time intervals 10-ml. aliquots were removed with a pipet and immediately delivered into a 125-ml. separatory funnel containing 10 ml. of 6 *M* HNO_3, 25 ml. of distilled water and 20 ml. of chloroform. The mixture was shaken thoroughly and the chloroform removed. The water layer was extracted further with another 20 ml. of chloroform. Finally the chloroform extracts were washed once with 5 ml. of water and the water layers combined. The bromide ion was determined by the Volhard method.

In calculating the rate constants the first sample was taken as the starting point of the reaction because solution of the bromoamide required 1–2 minutes of shaking. The release of bromide ion followed a second-order rate law over 70% of the reaction range, after which the velocity coefficients exhibited a slight downward drift.

Typical rate data for the reaction of N-*p*-chlorophenyl-4-bromobutanamide and N-phenyl-4-bro-

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[1] H. W. Heine and B. L. Kapur, THIS JOURNAL, **77**, 4892 (1955); H. W. Heine and W. Siegfried, **76**, 489 (1954); **75**, 4778 (1953); **75**, 4514 (1953); **73**, 1348 (1951).

[2] J. Tafel and M. Stern, *Ber.*, **33**, 2235 (1900).

[3] T. B. Baillie and J. Tafel, *ibid.*, **32**, 74 (1898)

mobutanamide with sodium methoxide are given in Table I. Table II summarizes the complete data on the various 4-bromobutanamides studied.

TABLE I

RATES OF ALKALINE SOLVOLYSIS OF N-ARYL-4-BROMOBUTANAMIDES AT 22.90°

0.0456 N $NaOCH_3$ Time, min.	Mmols Br^-/10 ml.	0.0456 N Bromoamide $k \times 10$, l. moles^{-1} min.$^{-1}$
N-p-Chlorophenyl-4-bromobutanamide		
4.59	0.048	5.62
8.97	.086	5.64
22.00	.166	5.68
35.83	.219	5.64
50.00	.258	5.68
61.83	.282	5.75
∞	.456	(Mean) 5.66
N-Phenyl-4-bromobutanamide		
0.1450 N $NaOCH_3$		0.0450 N Bromoamide
11.83	0.072	1.77
22.91	.128	1.81
34.75	.175	1.83
48.63	.219	1.83
68.46	.264	1.83
89.88	.298	1.79
∞	.450	(Mean) 1.81

TABLE II

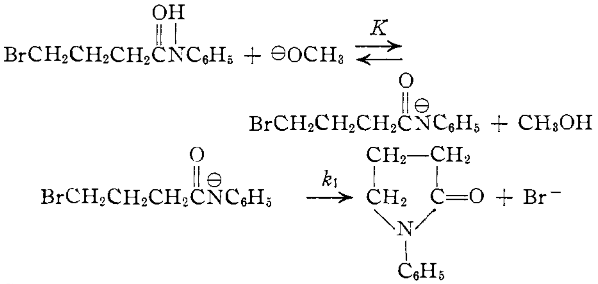
RATE CONSTANTS FOR THE ALKALINE SOLVOLYSES OF SOME N-ARYL-4-BROMOBUTANAMIDES AT 22.90°

N-Aryl-4-bromobutanamide	$NaOCH_3$, N	Amide, N	$k \times 10$, l. min.$^{-1}$ mole^{-1}
p-Chlorophenyl	0.0456	0.0456	5.66
	.0465	.0465	5.77
	.0938	.0438	5.57
	.0455	.0455	5.70
	.0897	.0397	5.63
	.0888	.0388	5.60
		(Mean)	5.65
Phenyl	0.0962	0.0462	1.80
	.1456	.0456	1.77
	.1452	.0452	1.79
	.0923	.0423	1.84
		(Mean)	1.80
p-Tolyl	0.1958	0.0458	1.02
	.1948	.0448	1.03
	.1963	.0463	1.03
		(Mean)	1.03

A few runs also were made without any base to establish that the reaction of the bromoamides with methanol was negligible compared to the reaction with methoxide ion. The values so obtained for N-p-chlorophenyl-, N-phenyl- and N-p-tolyl-4-bromobutanamides at 22.90° were 5.0, 7.8 and 8.8 $\times 10^{-4}$ min.$^{-1}$, respectively. It is to be observed that in the case of the N-p-chlorophenyl-4-bromobutanamide the reaction with methanol was of such magnitude as to make no appreciable contribution to the observed rates in alkaline solution. The first-order reaction of N-phenyl-4-bromobutanamide with solvent was also very slow but did make a slight contribution to the observed second-order rates when the concentration of base to amide was in a ratio of one to one. This difficulty was overcome simply by working at higher methoxide concentrations. In the case of the N-p-tolyl-4-bromobutanamide the first-order solvolysis competed with the second-order process to the extent of 6–10% when the concentration of base to amide was one to one. However, when the methoxide concentration was increased to four times the quantity of amide the second-order process had a half-life of approximately 35 minutes. Under these conditions the first-order process with a half-life of approximately 800 minutes becomes insignificant. It was also observed that the first-order constants drifted downward after approximately 30% of the reaction had been completed. This was attributed to the formation of halogen acid.

Discussion

A reaction mechanism in accord with the second-order kinetics as well as the formation of pyrrolidones as products would be a two-step process where the first step is a rapid reversible proton transfer between the methoxide ion and the N–H group, and the second, the unimolecular, rate determining intramolecular displacement of bromide ion by negatively charged nitrogen, *i.e.*



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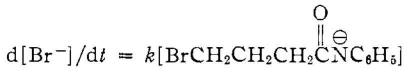
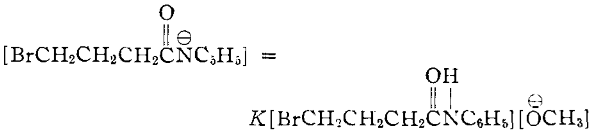


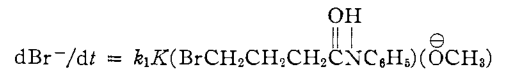
$$d[Br^-]/dt = k[BrCH_2CH_2CH_2\overset{\overset{O}{\|}}{C}\overset{\ominus}{N}C_6H_5]$$

and



$$[BrCH_2CH_2CH_2\overset{\overset{O}{\|}}{C}\overset{\ominus}{N}C_5H_5] = K[BrCH_2CH_2CH_2\overset{\overset{OH}{\|\ |}}{CN}C_6H_5][\overset{\ominus}{O}CH_3]$$

the rate of production of bromide ion is given by



$$dBr^-/dt = k_1K(BrCH_2CH_2CH_2\overset{\overset{OH}{\|\ |}}{CN}C_6H_5)(\overset{\ominus}{O}CH_3)$$

The observed second-order rate constant k is equal to k_1K and thus depends upon the reactivity of the formed bromoamido ion and the acidity of the bromoamide.

On the basis of the above formulation it is to be expected that introduction in the aryl system of groups capable of electron withdrawal would enhance the acidity (K) of the bromoamide and thereby increase the observed rate constant k. On the other hand, the basicity of the bromoamido ion would be lowered by the presence of electron-withdrawing groups and thus cause a decrease in k_1 and consequently the experimentally observed constant k. The values recorded in Table II show that the rate of cyclization of the N-p-chlorophenyl-4-bromobutanamide is 3 and 5.5 times as fast as 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}_{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

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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).