Both inductive and hyperconjugative effects for these substituents are positive causing them to be deactivating with respect to hydrogen.

The inductive effect should not be very different when the substituent is in *m*- or *p*-position, but hyperconjugation determines the order $k_{5\text{-R}} > k_{4\text{-R}}$ because it can only act directly when the alkyl group is in the *p*-position.

The ratio k_m/k_p for *t*-butyl, significantly greater than unity, suggests that for this substituent as well as for methyl, hyperconjugation plays an important role. These results agree with those of Capon and Chapman.[21]

The effects of the phenyl group cannot be interpreted for both positions of the substituent on the same basis of negative inductive and positive mesomeric effects.

Ingold[70] pointed out the variable capacity of the phenyl group to act as an electron acceptor or donor, depending on the reaction requirements, and the general structure to which it is attached.

De la Mare and Ridd[71] have recently discussed the influence of several factors on electrophilic substitutions in diphenyls and structurally related compounds. Berliner and co-workers[66,72] have established that transmission of polar effects of substituents through the diphenyl moiety is less intense than through benzene itself. In the activation of the chlorine atom by the phenyl group in 4-chloro-3-nitrobiphenyl, the negative inductive effect of the substituent is more powerful than the opposing mesomeric effect; but in 3-chloro-4-nitrobiphenyl, where the phenyl group is *para* to the nitro group, mesomeric interaction by *para*-conjugation operates with its consequent electronic release balancing the electron-attracting effect of the phenyl group.

In the conditions of our experiments the phenyl group slightly enhances the reactivity from the *m*-position (R.R. = 1.05); a greater increment is observed from the *p*-position (R.R. = 2.1).

Berliner and co-workers have obtained a similar result in the reaction of 4-bromo-3-nitrobiphenyl with piperidine in which this compound reacts 2.2 times as fast as *o*-bromonitrobenzene.

Brown, Okamoto and Inukai[73] found that the phenyl substituent, in the solvolysis of phenyldimethylcarbinyl chlorides system in which no nitro group is present, increases the rate by six times from the *p*-position while it is deactivating from the *m*-position (R.R. = 0.32). These results can be compared with those of Berliner and Shieh[74] for the solvolysis of α-phenylethyl chlorides in which they find that forcing both rings of the biphenyl moiety to be coplanar, by introduction of an *ortho–ortho* methylenic bridge (fluorenyl derivative), increases the rate of reaction by a factor of seven hundred.

Finally we wish to record from experiments made in this Laboratory by Miss Hebe B. Belmonte that it has not been possible to obtain 3-chloro-4-nitroazobenzene by condensation of nitrosobenzene with 3-chloro-4-nitroaniline and hence to study the polar effects of the *m*-phenylazo substituent in the reaction.

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[CONTRIBUTION FROM THE LABORATORIO DE QUIMICA ORGANICA, FACULTAD DE CIENCIAS EXACTAS Y NATURALES, UNIVERSIDAD NACIONAL DE BUENOS AIRES, BUENOS AIRES, ARGENTINA]

The *ortho:para* Ratio in the Activation of the Nucleophilic Aromatic Substitution by the Nitro Group

BY W. GREIZERSTEIN AND J. A. BRIEUX[1]

RECEIVED MAY 26, 1961

The amount of substitution of the chlorine atoms of 2,4-dichloronitrobenzene-4-Cl^{36} by piperidine in benzene and methanol has been determined by a radiochemical method. The results have been compared with the reactions of *o*- and *p*-chloronitrobenzene with piperidine in the same solvents and in ethanol. It is concluded that while the change from benzene to methanol lowers the over-all rate of substitution, it enhances selectively the reactivity of the chlorine atom *para* to the nitro group. Reaction kinetics are tentatively explained and Arrhenius parameters presented.

Bunnett and Zahler[2] and more recently Bunnett and Morath[3] have reviewed the extensive literature on the activating effect of the nitro group in aromatic nucleophilic substitution.

It is well known that in the series of nitro-halogenobenzenes, the *para* isomers are the more reactive with reagents that have lone pairs of electrons on an atom of Group VI of the periodic table, such as alkoxides, phenoxides, thiophenoxides, etc.,

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(1) Inquiries should be addressed to Laboratorio de Química Orgánica, Facultad de Ciencias Exactas y Naturales, Perú 272, Buenos Aires, Argentina.

(2) J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 273 (1951).

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TABLE I

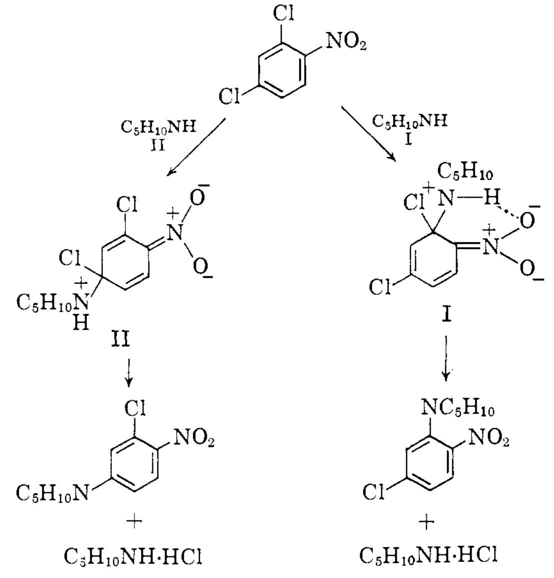
RATE COEFFICIENTS AND ARRHENIUS PARAMETERS FOR THE REACTIONS OF *o*- AND *p*-CHLORONITROBENZENES AND 2,4- AND 2,5-DICHLORONITROBENZENES WITH SODIUM METHOXIDE IN METHANOL,[4] DIETHYLAMINE IN METHANOL[4] AND PIPERIDINE IN BENZENE[5,7]

	Sodium methoxide in methanol[4]			Diethylamine in methanol[4]			Piperidine in benzene[5,7,a]		
Compound	$10^5 k_2$, l. mole^{-1} sec.$^{-1}$ at 85°	E, kcal./mole	ΔS^*, 85°	$10^7 k_2$, l. mole^{-1} sec.$^{-1}$ at 85°	E, kcal./mole	ΔS^* 85°	$10^7 k_2$, l. mole^{-1} sec.$^{-1}$ at 85°	E, kcal./mole	ΔS^*,
2-$ClC_6H_4NO_2$	10.3	22.8	−13.4	3.89	14.5	−48	439	13.9	−40
4-$ClC_6H_4NO_2$	38.5	23.1	−10.1	1.81	14.1	−50	7.97	13.7	−48
2,4-$Cl_2C_6H_3NO_2$	550	22.6	− 6.0	75.2	13.7	−44	8340	11.5	−41
2,5-$Cl_2C_6H_3NO_2$	108	23.0	− 8.0	18.8	13.4	−48	1860	12.1	−42

[a] These experiments were run with concentrations 0.1 *M* in halogen derivative and 1.0 *M* in amine.

while the *ortho* isomers are the most reactive with ammonia and amines. Holleman, de Mooy and ter Weel[4] have studied the reaction of 2,4- and 2,5-dichloronitrobenzene with sodium methoxide and diethylamine in methanol; Greizerstein, Bonelli and Brieux[5] examined the reaction of the same compounds with piperidine in benzene.

Table I summarizes the results of these previous studies, showing the activating effect of a chloro substituent both from the *p*- or *m*-position to the site of substitution, and also the greater rate of substitution of the chlorine *ortho* to the activating nitro group (reaction I).



Den Hertog and Jouwersma[6] in experiments of a preparative character found that 2,4-dichloronitrobenzene reacts quicker with ammonia in water, giving 2-amino-4-chloronitrobenzene and a small amount of 4-amino-2-chloronitrobenzene, than in ethanol in which only the former product is formed.

2,4-Dichloronitrobenzene has an adequate structure for study of the influence of several factors on activated aromatic nucleophilic substitution. With the purpose of increasing the information about some of these, 2,4-dichloronitrobenzene-4-Cl^{36} was synthesized and the experiments summarized in Tables II, III and IV were carried out.

The relative rates of displacement of the two chlorines from 2,4-dichloronitrobenzene-4-Cl^{36} and solvent effects on the relative rates of reaction of *o*- and *p*-chloronitrobenzene with piperidine were determined.

Experimental

Solvents and Reagents.—Benzene and piperidine were purified as described in the preceding paper.[5]

Anhydrous methanol and ethanol were made from 99% alcohols by the method of Lund and Bjerrum.[8]

The solutions of "mixed solvents," benzene–methanol and benzene–ethanol, were prepared independently for each experiment, by weighing the desired amount of alcohol in a 100-ml. flask with the reagents and filling to the mark with benzene.

o- and *p*-chloronitrobenzene were white label Eastman Kodak Co. products recrystallized from ethanol; m.p. 32° and 83.5–84°, respectively.

Cuprous Chloride.—The method used for its preparation is based on the procedure of Keller and Wycoff[9] modified by Meikle.[10] Hydrochloric acid-Cl^{36} (1.20 ml., 1.89 *N*, specific activity 0.296 μc./mmole)[11] was partially neutralized with 2.8 *N* sodium hydroxide to pH 5; then 574.2 mg. of copper sulfate pentahydrate analytical reagent grade was added and the resultant solution was heated nearly to boiling. A freshly prepared solution of sodium bisulfite, obtained by bubbling sulfur dioxide into 1.8 ml. of 2.8 *N* sodium hydroxide, was rapidly poured into the former hot solution. The precipitate thus formed was vigorously stirred until it turned white, then digested for 5 minutes on a water-bath, cooled to 0° and centrifuged. After decantation of the aqueous layer, the cuprous chloride was washed with water containing sulfur dioxide, and then successively, twice each time, with glacial acetic acid, absolute ethanol and anhydrous ether; centrifugation was used to separate the liquid phase; yield 200–205 mg.

2,4-Dichloronitrobenzene-4-Cl^{36}.—3-Chloro-4-nitroaniline (477 mg.) was diazotized as described in the previous paper.[5] The diazonium salt solution was poured into a solution of 203 mg. of cuprous chloride-Cl^{36} and 222 mg. of sodium chloride-Cl^{36} in 1.4 ml. of hydrochloric acid-Cl^{36}, 1.89 *N*. The product was left overnight and then steam distilled. After 12 hours in a refrigerator, it was filtered and dried; yield 393 mg., m.p. 30.5°. After two sublimations under reduced pressure (1–2 mm., 50°) 353 mg., m.p. 30.5–31.5°, was obtained. *Anal.* Calcd. for $C_6H_3O_2NCl_2$: N, 7.30. Found: N, 7.34.

***m*-Chloronitrobenzene-Cl^{36}.**—Following the details for the preparation of 2,4-dichloronitrobenzene described above, and using the same proportions, 2.190 g. of *m*-nitroaniline gave 1.309 g. of *m*-chloronitrobenzene, m.p. 44.5–45.5°, 90% yield with respect to cuprous chloride.

***m*-Chloroacetanilide-Cl^{36}.**—To 1.309 g. of *m*-chloronitrobenzene-Cl^{36} and 4.5 g. of granulated tin heated on a water-bath, 30 ml. of hydrochloric acid 18% was added. Heating

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(4) A. F. Holleman, W. J. de Mooy and J. ter Weel, *Rec. trav. chim.*, **35**, 1 (1915).

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(9) R. N. Keller and H. D. Wycoff, "Inorganic Syntheses," Vol. II, 1946, p. 1, W. C. Fernelius, Ed., McGraw-Hill Book Co. Inc.

(10) R. W. Meikle, *J. Org. Chem.*, **24**, 278 (1959).

(11) Obtained by dilution of the product, 116 μc./g. Cl, provided by Radiochemical Centre, Amersham, England, with isotopically normal hydrochloric acid.

TABLE II

REACTIONS OF 2,4-DICHLORONITROBENZENE AND 2,4-DICHLORONITROBENZENE-4-Cl^{36} WITH PIPERIDINE IN BENZENE AND METHANOL

	$2,4\text{-}Cl_2C_6H_3NO_2$										
Expt.	4-Cl, mg.	4-Cl^{36}, mg.	$C_5H_{10}NH$, g.	Solvent	Time, min.	NaCl added mg.	AgCl obtained mg.	C./min.	C./min./100 mg. of AgCl	% Cl^{36} in total Cl	% Cl subst.
	...	1.80	...	.....	..	41.8	103.5	1044	1015	1.28[a]	..
1	140.8	....	0.675	C_6H_6	385	..	...	..	..	..	48.3
2	...	144.0	.675	C_6H_6	385	..	103.0	600	582	0.73	
3	...	141.8	.675	C_6H_6	385	..	100.0	555	555	0.70	
4	151.9	....	.675	C_6H_6	385	..	...	..	..	..	48.6
	...	2.00	...	..	..	42.7	106.8	1130	1090[c]	1.38[b]	
	...	1.85	...	..	..	41.9	98.5	1083	1100	1.31[b]	
5	147.0	....	0.710	C_6H_6	285	..	...	..	..	..	49.7
6	...	140.7	1.528	C_6H_6	285	..	98.0	1482	1512	1.86	
7[f]	...	141.8	0.661	C_6H_6	415	..	101.7	842	828	1.01	
8[f]	147.4	....	0.672	C_6H_6	415	..	...	..	..	..	49.7
	...	1.90	...	..	..	41.9	103.0	1262	1222	1.36	
9	142.1	....	0.668	C_6H_6	387	..	...	..	..	..	48.5
10	...	142.6	.668	C_6H_6	387	..	102.8	653	636	0.69	
11	146.0	....	.671	CH_3OH	387	..	...	..	..	..	33.5
12	...	143.6	.671	CH_3OH	387	..	65.9	5637	7230[d]	7.95	
13	111.1	....	.548	CH_3OH	360	..	...	..	..	..	26.1
14	...	112.4	.548	CH_3OH	360	..	47.5	3875	6530[e]	7.18	

[a,b] Correspond, respectively, to 794 and 911 counts per minute per 100 mg. of silver chloride containing 1% of radioactive chloride in total chlorine. [c] To the counts per minute per 100 mg. of silver chloride a 3% correction for self absorption due to 6.8 mg. of silver chloride in excess over 100 mg. was made. [d,e] Corrections of 15.6% and 20% for self absorption were made to the counts per minute per 100 mg. since the amounts of precipitate were roughly two-thirds and half of 100 mg. [f] In experiments 6 and 7 the order of addition of reagents and/or their relative amount was changed; pure piperidine was added before the solvent.

was continued for 2 hours, 1 g. of granulated tin having been added after the first hour. The solution was alkalinized with ammonium hydroxide, filtered, and extracted with ether. The extract was dried with sodium sulfate and the solvent eliminated. The residue was treated with acetic anhydride, heated at 100° for 15 minutes, then poured on ice, and shaken for 12 hours at room temperature; yield 0.964 g., m.p. 71–72.5°.

3-Chloro-4-nitroacetanilide-Cl^{36} and 3-Chloro-6-nitroacetanilide-Cl^{36}.—The procedure of Fourneau, Tréfouel, Tréfouel and Wancolle,[12] when starting with 0.964 g. of *m*-chloroacetanilide-Cl^{36}, yielded 0.520 g. of 3-chloro-4-nitroacetanilide-Cl^{36}, m.p. 143–144°, and 0.473 g. of 3-chloro-6-nitroacetanilide-Cl^{36}, m.p. 118–120°.

3-Chloro-4-nitroaniline-Cl^{36}.—3-Chloro-4-nitroacetanilide-Cl^{36} (0.520 g.), refluxed for 30 minutes with 6 ml. of 18% hydrochloric acid and quenched in 20 ml. of water, gave 0.393 g. of 3-chloro-4-nitroaniline-Cl^{36}, m.p. 157–158°.

2,4-Dichloronitrobenzene-2-Cl^{36}.—A solution of 39 mg. of 3-chloro-4-nitroaniline-Cl^{36}, specific activity 1 μc./mmole, in 0.3 ml. of glacial acetic acid was diazotized with 17.6 mg. of sodium nitrite in 0.3 ml. of concentrated sulfuric acid. The diazonium salt was poured into a solution of 22.5 mg. of cuprous chloride, and 24.7 mg. of sodium chloride in 0.16 ml. of 1.89 *N* hydrochloric acid. After standing overnight, the product was extracted three times with 15 ml. of hot benzene. From the benzene extracts 34.4 mg. of 2,4-dichloronitrobenzene, 2-Cl^{36} was obtained.

The aqueous layer was acidified and treated with 11 ml. of 0.07 *N* silver nitrate solution, proceeding afterward as detailed in the experiments with radioactive chloride; 105 mg. of silver chloride was obtained that registered 196 counts per minute.

The average of the mineralizations of the 2,4-dichloronitrobenzene-4-Cl^{36} (specific activity 0.296 μc./mmole) show that for an activity of 1 μc./mmole would correspond 2777 counts per minute for a 100 mg. of silver chloride sample. These data show that except for errors by adsorption of organic material on the silver chloride obtained from the residual aqueous medium of the Sandmeyer reaction, 4.75×10^{-4} mmole of radioactive chlorine, from the original 2.27×10^{-1} mmole of 3-chloro-4-nitroaniline-Cl^{36} (1 μc/mmole), have passed, as a maximum, as chloride ion to the reaction medium; consequently not more than 0.21% of the chlorine of the amine could have been substituted by chloride ion or any other nucleophile from the medium.

The silver chloride was dissolved in ammonia, extracted again three times with benzene and reprecipitated with nitric acid. This treatment was repeated once more. Data for exchange were, respectively, 0.12 and 0.18%.

Kinetic Runs.—For experiments with *o*- and *p*-chloronitrobenzene the technique described in the previous paper was used.

Quantitative Radiochemical Experiments.—In the experiments with 2,4-dichloronitrobenzene-4-Cl^{36} a 10-ml. volumetric flask containing 140.7 mg. of 2,4-dichloronitrobenzene-4-Cl^{36} was filled to the mark with a 0.7 *M* solution of piperidine in benzene or methanol. The flask was placed in a thermostat at 60 ± 0.1° for a period of time calculated to obtain the desired conversion by a parallel experiment with non-radioactive 2,4-dichloronitrobenzene.

The radiochemical measurements were performed on the silver chloride obtained after quenching the reaction solutions in dilute nitric acid. In the case of benzene solutions, the benzene layer was rejected; methanolic solutions were extracted with benzene and this rejected. The aqueous layer was treated with 11 ml. of 0.07 *N* silver nitrate, heated to boiling with vigorous stirring, and left overnight. Silver chloride was filtered using filter paper Schleicher and Schüll 589^3, and washed successively with water, twice with absolute alcohol and twice with anhydrous ether, pressing the precipitate adequately to obtain uniform surface and thickness.

The dried precipitate was weighed with the filter paper, and the weight of another filter paper, subjected simultaneously to the same treatment, was subtracted. The silver chloride with the paper was placed in an aluminum box and its activity determined with a Geiger-Müller tube.

A reference standard was obtained by mineralizing about 2 mg. of 2,4-dichloronitrobenzene-4-Cl^{36} by the method of Schöniger,[13] and adding the amount of non-radioactive sodium chloride necessary to have, after treatment of the solution as described above, 100 mg. of silver chloride. The introduction of a correction for self-absorption was considered more convenient than the handling of smaller samples.

Table II summarizes the experimental data.

The precision of the method was checked by preparing standards containing 1, 3 and 7% radioactive chlorine.

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[12] E. Fourneau, J. Tréfouel, Mme. J. Tréfouel and A. Wancolle, *Bull. soc. chim. France*, [4] **47**, 743 (1930).

[13] W. Schöniger, *Mikrochim. Acta*, 123 (1955).

The experimental results were 1.09, 3.04 and 7.01%.

The autoabsorption curve was determined. For 5, 10 and 25 mg. of silver chloride the counts per minute remained constant, while precipitates weighing 50, 100 and 150 mg., diminished the counting by 10, 30 and 40%, respectively; surface was kept constant throughout.

The efficiency of the Geiger–Müller tube used was 18%.

Discussion

The results from experiments 2, 3 and 10 in Table II show that only 0.7% of the substituted chlorine in the reaction of 2,4-dichloronitrobenzene with piperidine in benzene originates in the position *para* to the nitro group.

This small percentage of displacement by the nucleophile of radioactive chlorine in 2,4-dichloronitrobenzene-4-Cl^{36} leads to the questions of the radiochemical purity of the compound and whether it really comes from substitution of halogen at the 4-position. The experiments described in connection with the preparation of 2,4-dichloronitrobenzene-2-Cl^{36} provide affirmative answers to both questions, as they show that the exchange of chlorine in the 2-position during its preparation by the Sandmeyer reaction on 3-chloro-4-nitroaniline is smaller than 0.21%.

In experiments 6 and 7 the order of addition of reagents and their relative amount was changed. Pure piperidine was added to the substrate before the solvent, having thus at first a solution of the chlorine compound in piperidine. These results are in agreement with the important role played by solvent composition on the *ortho:para* ratio found by other workers.

This was confirmed by experiments 11, 12, 13, and 14 in which methanol was used as solvent. The over-all rate of substitution in this case is smaller, but the reactivity of the *p*-position is sensibly enhanced. While in benzene, 48.5% of the total chlorine is replaced, 0.7% coming from the *p*-position, in the same experimental conditions in methanol, only 33.5% of chlorine is substituted, of which 8% comes from the *p*-position. An analogous influence is noted in the rates and Arrhenius parameters for the reaction of *o*- and *p*-chloronitrobenzene with piperidine in benzene, methanol and ethanol summarized in Table III and in the rates for the reaction of these same compounds with piperidine, in mixed solvents benzene–methanol (Table IV).

TABLE III

REACTIONS OF *o*- AND *p*-CHLORONITROBENZENE WITH PIPERIDINE[a]

Compound	Solvent	$k_2 \times 10^7$, l. mole^{-1} sec.$^{-1}$ 60°	75°	100°	*E*, kcal. mole^{-1}	$\Delta S^*_{75°}$ e.u.
2-$ClC_6H_4NO_2$	Benzene	105	239	903	13.4	−41
	Methanol	23.3	75.7	413	18.0	−31
	Ethanol	29.2	90.0	481	17.9	−31
4-$ClC_6H_4NO_2$	Benzene	1.77	3.89	13.9	13.0	−51
	Methanol	10.6	35.8	168	16.7	−36
	Ethanol	13.1	38.2	182	16.6	−36

[a] These experiments were run with a ratio of halogen derivative to piperidine of 0.07 *M*/0.7 *M*.

From comparison of Tables I and III, it can be observed that for reactions of *p*-chloronitrobenzene with piperidine in benzene, which differ only in the molarity of the reagents, there are differences in rate that are well outside experimental error.

TABLE IV

INFLUENCE OF THE "MIXED SOLVENT" BENZENE–METHANOL UPON THE RATE OF REACTION OF *o*- AND *p*-CHLORONITROBENZENE WITH PIPERIDINE[a]

Nitrobenzene	$k_2 \times 10^7$ l. mole^{-1} sec.$^{-1}$ at 100° — % of methanol in benzene 0	0.15	5	15	25	50	75	100
2-Chloro-	903	868	646	625	507	406	387	413
4-Chloro-	13.9				60.5	102	131	168
k_o/k_p	65				8.4	4.0	3.0	2.2

[a] These experiments were run with a ratio of halogen derivative to piperidine of 0.07 *M*/0.7 *M*.

The 10% increase in rate when the concentration of piperidine goes from 0.7 to 1.0 *M* shows the greater sensibility to changes in the composition of solvent of intermediate complexes of type II relative to those of type I.

This greater sensibility shows as well in the ratio k_o/k_p (Table IV), which is thirty times greater for the reactions in benzene than in methanol. The cause is more a tenfold increase of the rate of *p*-chloronitrobenzene, rather than the small decrease of the rate of *o*-chloronitrobenzene, when changing from the former to the latter solvent.

The order of reactivity is reversed for the reaction with sodium methoxide in methanol.

Table I shows that for a given pair of solvent and nucleophile, energies of activation for *o*- and *p*-chloronitrobenzene are very similar. The entropies of activation are the factors that determine the differences in reactivity.

For the reactions with amines in non-polar solvents, the ratio k_o/k_p is about 50–80[7,14] and the energy of activation about 13–14 kcal. mole^{-1}; for alcoholic solutions of amines k_o/k_p is smaller but remains greater than unity[4]; with alkoxides in alcohol the ratio k_o/k_p is less than unity and the energy of activation greater than 20 kcal. mole.[4,15,16]

Methanol has, in addition to its amphiprotic character defined by eq. III, a capacity for solvation by coördination through its lone pairs of electrons on the oxygen atom and by hydrogen bonding with the oxygen atoms of the activating nitro group. Piperidine shows similar effects in its solvating actions.

$$C_5H_{10}NH + CH_3OH \rightleftarrows CH_3O^- + C_5H_{10}NH_2^+ \quad (III)$$

These effects of the solvents superimposed to the "self solvation" between the positive and negative centers in the activated complex, claimed by Bunnett and Morath[3] to explain the order *ortho* > *para* in reactions of chloronitrobenzenes with amines, would be the determining factors of the differences in reactivity observed.

The equilibrium III apparently is not kinetically important as shown by the general experience that no ethers were ever isolated in the reactions of halogen–nitrobenzenes with amines in alcoholic solutions. Cavell and Chapman[17] have examined Bunnett and Zahler's suggestion[18] that ethanolysis may intervene in reactions of the type we have studied, concluding that the intervention of ethanolysis is unlikely.

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(14) M. F. Hawthorne, *J. Am. Chem. Soc.*, **76**, 6358 (1954).

(15) J. Miller, *J. Chem. Soc.*, 3550 (1952).

(16) C. W. L. Bevan, *ibid.*, 2340 (1951).

(17) E. A. S. Cavell and N. B. Chapman, *ibid.*, 3392 (1953).

(18) See ref. 2, p. 344.

Hamann and Straus[19] have determined equilibrium constants at 25° and 45° for reaction III, finding the values: $K_{25°} = 6.1 \times 10^{-6}$ mole kg.$^{-1}$ and $K_{45°} = 2.8 \times 10^{-6}$ mole kg.$^{-1}$ for $K = (a_{C_5H_{10}NH_2^+}) \times (a_{CH_3O^-})/(a_{C_5H_{10}NH})$ in which a are molal activities.

For pure piperidine, $a_{C_5H_{10}NH} \cong 11.7$ mole kg.$^{-1}$; hence for solutions of piperidine in methanol such as those employed in experiments of Table III, this term is smaller and therefore $a_{CH_3O^-}$ at 45° is smaller than $[K(a_{C_5H_{10}NH})]^{1/2} = [2.8 \times 10^{-6} \times 11.7]^{1/2} = 5.7 \times 10^{-3}$ mole kg.$^{-1}$. From this figure and from the known rates of reaction of *o*- and *p*-chloronitrobenzenes with sodium methoxide in methanol (Table I) and with piperidine in the same solvent (Table III), it can be seen that aminolysis is the only reaction that takes place under the experimental conditions of Table III, due to the very low concentration of methoxide ion.

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[19] S. D. Hamann and W. Straus, *Disc. Faraday Soc.*, **22**, 70 (1956).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF VERMONT, BURLINGTON, VT.]

Ionic Reactions in the Spirane Series. I. Effect of Adjacent Ring Size on the Acetolysis of Neopentyl-type Tosylates of the Spirane Series

BY A. PAUL KRAPCHO AND MERRILL BENSON

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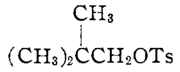
The acetolysis of several spirane tosylates (VI, $n = 2$, 3 and 4) of the neopentyl-type has been studied. The acetolysis rate was found to be dependent on adjacent ring size and the products of the acetolysis were predominantly olefins resulting from rearrangement. The results are discussed in terms of the effect of ring strain on anchimeric assistance in rearrangements of the Wagner–Meerwein type.

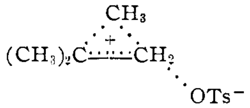
Introduction.—The Wagner–Meerwein rearrangement of neopentyl-type systems (I) to *t*-amyl systems (II) under solvolytic conditions has been investigated.[1] The fact that the formolysis of neopentyl tosylate is as rapid as that of ethyl tosylate has been attributed to anchimeric assistance of the neighboring methyl group and the transition state would have a bridged-ion structure (III).[2] The acetolysis of *cis*- and *trans*-9-decalylcarbinyl tosylates (IV and V), which represent a neopentyl system wherein the migrating group is an integral part of a fused ring system, has been investigated by Dauben.[3] These compounds solvolyze at the same rate at 90° and are five times faster than neopentyl tosylate, corresponding to a slight rate enhancement. The product in each case is predominantly the rearranged olefin and bridged-ion transition states are proposed.


$(CH_3)_2C(CH_3)CH_2OTs$

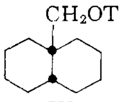
I

$(CH_3)_2\overset{+}{C}CH_2CH_3$

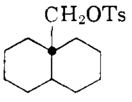
II



III



IV



V

It has also been reported that cyclopropylcarbinyl sulfonate and methylcyclobutylcarbinyl brosylate undergo solvolysis under ionizing conditions at rates which exceed those for non-cyclic substrates by factors of several hundred or more.[1,4] Here it is probable that the solvolysis is being assisted by a combination of field and anchimeric effects due to the neighboring cyclopropyl and cyclobutyl groups.

The favorable geometry of spirane tosylates (VI), in which the neopentyl system is also part of an alicyclic ring, seems well suited for a systematic study designed to assess ring strain *versus* anchimeric assistance as a driving force in rearrangements of the Wagner–Meerwein type.[5] The dehydration with accompanying rearrangement of spiranols has been the subject of many investigations.[6]

In order to obtain some preliminary information with regard to the effect of ring strain, the acetolysis rates of the spirane tosylate systems (VI) were investigated where $n = 2$, 3 and 4. As a model system the acetolysis rate of 2,2-dimethylcyclopentyl tosylate (VII) was measured for comparative purposes.

Synthesis.—The preparation of the spiranols followed standard routes previously described in

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[1] A. Streitwieser, Jr., *Chem. Revs.*, **56**, 571 (1956).

[2] S. Winstein and H. Marshall, *J. Am. Chem. Soc.*, **74**, 1120 (1952).

[3] W. G. Dauben and J. B. Rogan, *ibid.*, **79**, 5002 (1957).

[4] E. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., Inc., New York, N. Y., 1959, pp. 588–591, and references cited therein.

[5] S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber and J. Corse, *J. Am. Chem. Soc.*, **74**, 1113 (1952).

[6] (a) P. A. Naro and J. A. Dixon, *ibid.*, **81**, 1681 (1959), and references cited therein; (b) A. C. Cope, J. M. Grisar and P. E. Peterson, *ibid.*, **82**, 4299 (1960).