[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF REED COLLEGE AND THE UNIVERSITY OF NORTH CAROLINA]

Activation of the Nucleophilic Displacement of Chlorine from 4-Substituted-2-nitrochlorobenzenes and 4-Substituted-2,6-dinitrochlorobenzenes by Methoxide Ion[1,2]

BY J. F. BUNNETT, HENRY MOE AND DAVID KNUTSON

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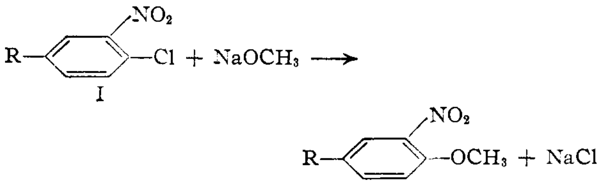
Rates of reactions of sodium methoxide with 4-substituted-2-nitrochlorobenzenes (I) and 4-substituted-2,6-dinitrochlorobenzenes (II) have been determined in order to assess the activating or deactivating effects of the 4-substituents. In reactions of I, the order of activating power is: $NO_2 > CH_3SO_2 > (CH_3)_3N^+ > CH_3CO > CF_3 > C_6H_5N_2$; in reactions of II, it is: $Cl > C_6H_5 > H > CH_3 > OCH_3$. The Hammett equation is obeyed except for deviations due to exceptional entropies of activation.

The activating effects of substituent groups toward aromatic nucleophilic substitution reactions have received increasing attention in recent years. Since this subject was reviewed[3] in 1951, several papers[4-11] have appeared dealing with various phases of it. The present paper is a direct continuation of an earlier contribution.[4]

Reactions of 4-Substituted-2-nitrochlorobenzenes with Sodium Methoxide.—In the present work, reactions of two additional compounds of structure I, in which the 4-substituent (R) is trifluoromethyl or phenylazo, have been studied. Earlier qualitative studies[12-14] showed that these two groups are moderately activating toward aromatic nucleophilic substitution, but did not provide accurate numerical assignments of their activating effects. Our work provides such assignments, as shown in Table I; this table includes similar data from an earlier study[4] for easy comparison.


I

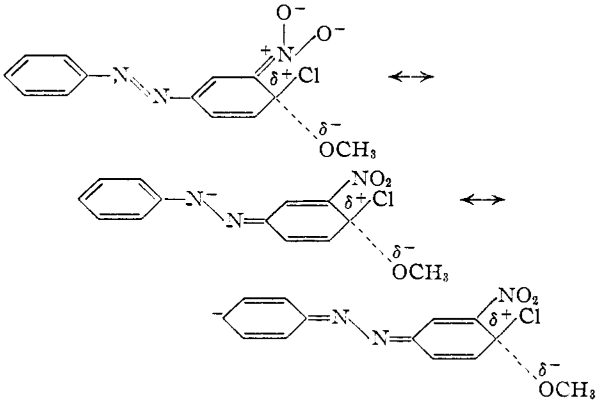
A glance at Table I reveals that two groups, trimethylammonio and phenylazo, are out of the order of reactivity to be expected from consideration of activation energies alone. This means that the corresponding entropies of activation are exceptional, and indeed, except for reactions activated by these two groups, all the entropies of activation in Table I fall in the range −9.6 to −12.3 cal./deg. For the reaction activated by trimethylammonio, the entropy of activation is high, apparently because of the special polar classification of this reaction,[4] while for reaction of the phenylazo compound (I, R = $C_6H_5N_2$), it is abnormally low. The exceptionally low entropy of activation is attributed to two effects. Let us consider the transition state[15] for the reaction which may be represented as

TABLE I

REACTIONS OF 4-SUBSTITUTED-2-NITROCHLOROBENZENES WITH SODIUM METHOXIDE IN METHANOL

Group in 4-position	Rate coefficient at 45.0°, l. mole^{-1} min.$^{-1}$	ΔE, kcal./mole	$\Delta S^{\ddagger}$, cal./deg.
NO_2[a]	8.71	16.8	−11.3
CH_3SO_2[b]	1.15	18.6	− 9.7
$(CH_3)_3N^+$[b]	0.428	20.3	− 6.3
CH_3CO[b]	.142	19.1	−12.3
CF_3[c]	.0803	20.4	− 9.6
$C_6H_5N_2$[c]	.0407	19.1	−15.2

[a] Calculated from literature values; *cf.* ref. 3, pp. 353 and 357. [b] From ref. 4. [c] Present investigation.



The first effect concerns the fact that the entire system of two benzene rings and the azo bridge must be coplanar in the transition state in order for resonance to occur as shown. This is in contrast to the initial state in which considerable twisting about carbon–nitrogen bonds may occur. The restriction of this twisting on formation of the transition state entails a loss of entropy, and this loss is

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[1] Presented to the Southern Regional Conclave, American Chemical Society, New Orleans, La., December, 1953.

[2] We are grateful to the U. S. Army, Office of Ordnance Research, for providing financial support of this research at both institutions.

[3] J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 307 (1951).

[4] J. F. Bunnett, F. Draper, P. R. Ryason, P. Noble, R. G. Tonkyn and R. E. Zahler, THIS JOURNAL, **75**, 642 (1953).

[5] E. Berliner and L. C. Monack, *ibid.*, **74**, 1574 (1952).

[6] C. W. L. Bevan, *J. Chem. Soc.*, 655 (1953).

[7] C. W. L. Bevan and G. C. Bye, *Chemistry and Industry*, 981 (1952).

[8] J. Miller, *J. Chem. Soc.*, 3550 (1952).

[9] M. Liveris, P. G. Lutz and J. Miller, *Chemistry and Industry*, 1222 (1952).

[10] J. Miller and V. A. Williams, *J. Chem. Soc.*, 1475 (1953).

[11] R. L. Heppolette and J. Miller, THIS JOURNAL, **75**, 4265 (1953).

[12] W. Borsche and I. Exss, *Ber.*, **56**, 2353 (1923).

[13] G. M. Badger, J. W. Cook and W. P. Vidal, *J. Chem. Soc.*, 1109 (1947); O. Galmarini, *Anales asoc. quim. argentina*, **38**, 19 (1950).

[14] E. T. McBee, R. O. Bolt, P. J. Graham and R. F. Tebbe, THIS JOURNAL, **69**, 947 (1947); J. F. Bunnett and A. Levitt, *ibid.*, **70**, 2778 (1948).

[15] This representation of the condition of bonding at the site of reaction is somewhat different from that used earlier (ref. 3, p. 300), but is intended to convey the same meaning. The dotted line with partial positive and negative charges on nuclear carbon and entering reagent, respectively, is meant to indicate a bond of partial covalent, partial ionic character.

greater than the loss when, for example, nitro or trifluoromethyl is the activating group. The second effect takes account of the fact that, because the phenylazo group is so large, there is exceptional opportunity for stabilization of its negative charge (in the transition state) by solvation. There is simply more room for solvent molecules about such a large group. This "freezing" of additional solvent molecules in the transition state lowers the entropy of activation.[16]

Figure 1 is a Hammett plot in which log $k_{45°}$ is plotted *vs.* σ^*.[17,18] It should be noted that the point for trimethylammonio lies above the line which has been drawn, while that for phenylazo lies practically on the line. The slope of the line ρ for the reaction is +3.97, about the same as derived earlier[4] from data available at that time.

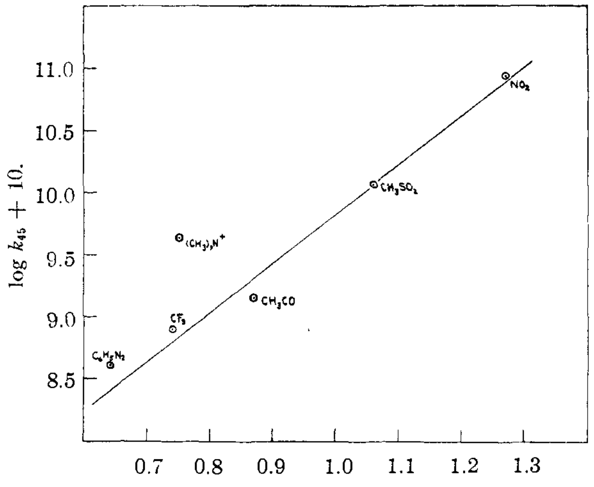


Fig. 1.—Plot of log k_{45} *vs.* Hammett σ-values, reactions of 4-substituted-2-nitrochlorobenzenes with sodium methoxide. The line was derived from the points for NO_2, CH_3SO_2, CH_3CO and CF_3 by the method of least squares.

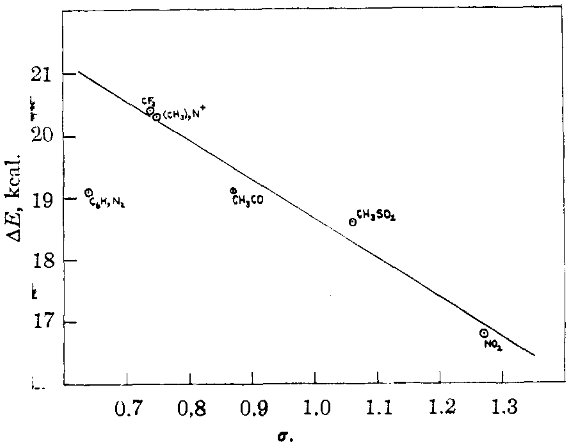
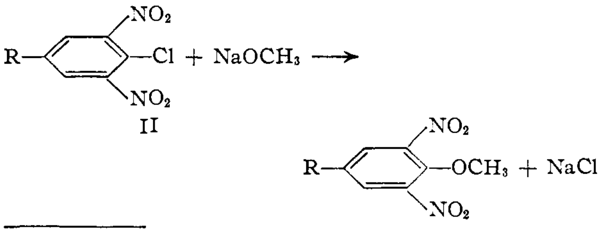


Fig. 2.—Plot of ΔE *vs.* Hammett σ-values, reactions of 4-substituted-2-nitrochlorobenzenes with sodium methoxide. The line was derived from all points except that for phenylazo by the method of least squares.

In Fig. 2, ΔE is plotted *vs.* σ^*. Since σ^* is expected to be closely related to enthalpy changes,[17] such a plot should bring reactions with exceptional entropies of reaction into line. Indeed, the point for trimethylammonio now falls nicely into line, but that for phenylazo is now out of line. This is a remarkable situation: the reactivity of the phenylazo compound is successfully correlated by a conventional Hammett plot, but not by a plot of ΔE *vs.* σ^*, which should give a better correlation. We believe the fault is in the σ-value used: a plain σ-value, based on the dissociation of *p*-phenylazobenzoic acid. Instead, a σ^*-value (+0.93) should be used so as to bring the phenylazo point into line in Fig. 2. The position of the phenylazo point in Fig. 1 is regarded as fortuitous; indeed, one should not expect a good Hammett correlation for a reaction with an exceptional entropy of activation.[20]

Quite apart from the present experimental evidence, one would have expected that a special σ^*-value for *p*-phenylazo would be necessary for successful correlation of reactions of anilines and phenols,[21] and of aromatic nucleophilic substitution reactions. The electronic characteristics of the phenylazo group are similar to those of other groups which do require the use of special σ^*-values.

Reactions of 4-Substituted-2,6-dinitrochlorobenzenes with Sodium Methoxide.—The reactions of five compounds of structure II, in which R is Cl, C_6H_5, H, CH_3 or OCH_3, have also been studied. In this series, there are two nitro groups *ortho* to the replaceable chlorine atom to provide initial activation, and so it is possible to obtain measurable rates of reaction at moderate temperatures when the group in the 4-position is weakly activating or even deactivating. Our results are summarized in Table II.



II

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[16] R. G. Pearson, *J. Chem. Phys.*, **20**, 1478 (1952).

[17] H. H. Jaffe, *Chem. Revs.*, **53**, 191 (1953).

[18] σ^* values were taken from ref. 17 except as follows: for $(CH_3)_3N^+$, +0.75 (ref. 19a); for CF_3, +0.74 (ref. 19b). The latter were chosen because they relate to the ionization of anilines and phenols, reactions from which σ^*-values generally are derived; Jaffe[17] did not list σ^*-constants for $(CH_3)_3N^+$ and CF_3. The plain σ-value was used for phenylazo since data from which to derive a σ^*-value were not found in the literature.

[19] (a) J. D. Roberts, R. A. Clement and J. J. Drysdale, THIS JOURNAL, **73**, 2181 (1951), (b) J. D. Roberts, R. L. Webb and E. A. McElhill, *ibid.*, **72**, 408 (1950).

[20] An alternative explanation of the paradox is that the position of the phenylazo point in Fig. 1 is correct and that its position in Fig. 2 is wrong owing to experimental error in determining the energy of activation. Now it is true that rate coefficients were determined for this reaction at only two temperatures, and those only ten degrees apart. However, at each temperature the determination was precise, and the reaction was in all respects well-behaved: plots of $1/(a - x)$ *vs.* t were in all cases strictly linear, methoxide consumption checked *vs.* chloride release, and the expected product was isolated. Therefore we have confidence in the activation energy value.

[21] Recently, L. L. Ingraham, J. Corse, G. F. Bailey and F. Stitt, THIS JOURNAL, **74**, 2297 (1952), used the plain σ-value to correlate the O–H stretching frequency of *p*-phenylazophenol. Also, J. L. Everett, J. J. Roberts and W. C. J. Ross, *J. Chem. Soc.*, 2386 (1953), used the plain σ-value to correlate the rate of hydrolysis of N,N-di-2-chloroethyl-*p*-aminoazobenzene. However, in both cases the correlation would have been as good had the new σ^*-value been used.

TABLE II

REACTIONS OF 4-SUBSTITUTED-2,6-DINITROCHLOROBENZENES WITH SODIUM METHOXIDE IN METHANOL

Group in 4-position	Rate coefficient at 45°, l. mole^{-1} min.$^{-1}$	ΔE, kcal./mole	$\Delta S^{\ddagger}$, cal./deg.
Cl[a]	2.29[b]	17.2	−12.9
C_6H_5	0.461	18.4	−12.6
H[c]	.292	18.0	−14.6
CH_3[d]	.0440	20.1	−11.9
OCH_3	.0043[b,e]	(22.7)[e]	(− 8.4)[e]

[a] From Miller and Williams,[10] k_{45} = 2.89 l. mole^{-1} min.$^{-1}$ (by calculation). ΔE = 17.4 kcal./mole. [b] Extrapolated from measurements at other temperatures. [c] From ref. 10, k_{45} = 0.374 l. mole^{-1}min.$^{-1}$ (by calculation), ΔE = 19.8 kcal./mole. [d] From ref. 10, k_{45} = 0.0457 l. mole^{-1} min.$^{-1}$ (by calculation), ΔE = 19.2 kcal./mole. [e] Since the rate determinations on this methoxy compound were not very satisfactory little confidence should be placed in the Arrhenius parameters.

In Fig. 3, log $k_{45°}$ is plotted against σ. The points fall nearly on a line, except that the methoxy point is off, as is frequently the case. The point for *p*-phenyl is somewhat out of line, but would fall nicely in line if a σ-value of +0.055 were used; Berliner and Liu[22] have emphasized that the electrical effect of the *p*-phenyl group varies from one reaction to another, requiring σ-values ranging from small negative values to as high as +0.419. ρ for this reaction is about +4.3, slightly higher than ρ for the reactions of compounds I with sodium methoxide.

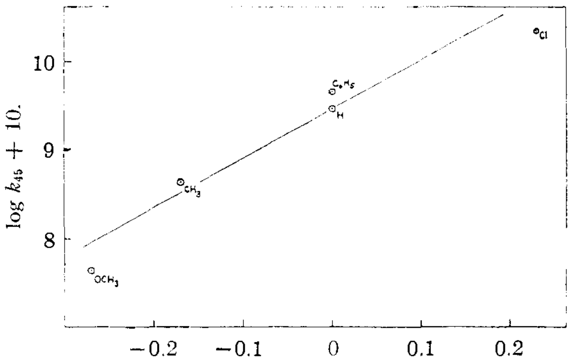

Fig. 3.—Plot of log k_{45} *vs.* Hammett σ values, reactions of 4-substituted-2,6-dinitrochlorobenzenes with sodium methoxide.

In the footnotes to Table II, some measurements on the same reactions by Miller and Williams[10] are recorded. Throughout, their rate coefficients ran higher than ours by as much as 20% or more. Also, two of their energies of activation are signficantly different from ours.

Such disagreement is disturbing. It happens that there are available, in two cases, independent determinations of rate coefficients with which our values and those of Miller and Williams can be compared. The comparisons are made in Table III. In both cases, we and the Dutch workers (working in the laboratory of A. F. Holleman) agree practically within experimental error, while Miller and Williams are about 20% high. The agreement increases confidence in both our work and the Dutch results. This is especially significant because it indicates that the large number of rate measurements on aromatic nucleophilic substitution reactions made in the laboratory of A. F. Holleman some twenty to forty years ago may be accepted as equivalent to good modern measurements. On the other hand, the aberrance of Miller and Williams' values suggests that they may have been troubled by a systematic error causing their measurements to run about 20% high.

TABLE III

COMPARISON OF RATE COEFFICIENTS FROM DIFFERENT LABORATORIES

Compound reacting	Temp., °C.	Rate coefficient, l. mole^{-1} min.$^{-1}$[a] Present work	Dutch workers	Miller and Williams[10]
2,4-Dinitrochlorobenzene	25.0	1.47[b]	1.50[c]	1.78
1,4-Dichloro-2,6-dinitrobenzene	0.0	0.0256	0.0248[d]	0.0311

[a] All reactions are with sodium methoxide in methanol. [b] Calculated from data at 25.19°, using an activation energy of 16.8 kcal./mole (ref. 3, p. 361); this coefficient was determined specifically to check our work against the Dutch determinations. [c] Average of several independent determinations, summarized in ref. 3, p. 357. [d] A. F. Holleman, *Rec. trav. chim.*, 39, 435 (1920).

Experimental

Synthesis of Compounds for Study. 4-Chloro-3,5-dinitrobiphenyl was prepared by the method of Borrows, Clayton, Hems and Long.[23] From 62.4 g. of 3,5-dinitro-4-hydroxybiphenyl,[24] 600 cc. of diethylaniline and 360 cc. of phosphorus oxychloride, a crude product was obtained. After removal of dark impurities by passing it (in benzene solution) through an alumina column, and then recrystallization from an acetone-ethanol mixture, 36 g. (54%) of 4-chloro-3,5-dinitrobiphenyl, m.p. 155–156°, were obtained as straw-colored crystals.[25]

Anal. Calcd. for $C_{12}H_7ClN_2O_4$: C, 51.72; H, 2.53. Found[26]: C, 52.09; H, 2.72.

The compound is very soluble in acetone but sparingly soluble in ethanol.

4-Chloro-3,5-dinitrotoluene.—In accord with the experience of Borrows, Clayton, Hems and Long,[23] we were able to obtain only poor yields (10 to 20%) by treating 2,6-dinitro-4-methylphenol[27] with phosphorus oxychloride and diethylaniline. The stepwise procedure of Borsche and Feske,[28a] wherein the dinitrophenol is converted to its *p*-toluenesulfonate ester, thence to a dinitroarylpyridinium *p*-toluenesulfonate by reaction with pyridine, and finally to the dinitroaryl chloride by treatment with an ionic chloride, was found to be more satisfactory for preparative purposes. In the final step of their procedure, Borsche and Feske heated the pyridinium salt with 5 *M* hydrochloric acid for 16 hours at 160–200°, and obtained the desired aryl chloride in unspecified yield. The following procedure is better: Seventy grams of 2,6-dinitro-4-methylphenylpyridinium *p*-toluenesulfonate, m.p. 179°, 600 g. of magnesium chloride hexahydrate and 1000 cc. of caproic acid were mixed and heated with stirring in a distilling apparatus. The distillate which boiled below 170° was discarded, and

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(22) E. Berliner and L. H. Liu, THIS JOURNAL, **75**, 2417 (1953).

(23) E. T. Borrows, J. C. Clayton, B. A. Hems and A. G. Long, *J. Chem. Soc.*, S190 (1949).

(24) A. G. Banus and J. Guiteras, *Anal. soc. espan. fis. quim.*, **21**, 126 (1922), *C. A.*, **17**, 2574 (1923).

(25) A. B. Sen, *J. Indian Chem. Soc.*, **22**, 183 (1945), *C. A.*, **40**, 5417 (1946), reported m.p. 111° for this compound. Since he reported m.p. 158° for the *p*-toluenesulfonate ester of 3,5-dinitro-4-hydroxybiphenyl, it seems possible that he may have confused the identity of his samples.

(26) Analysis by Clark Microanalytical Laboratory, Urbana, Ill.

(27) E. Baroni and W. Kleinau, *Monatsh.*, **68**, 251 (1936).

(28) (a) W. Borsche and E. Feske, *Ber.*, **60**, 159 (1927): (b) W. Borsche and D. Rantscheff, *Ann.*, **379**, 152 (1911).

then the apparatus was arranged for reflux and the mixture was refluxed two hours. The product, 4-chloro-3,5-dinitrotoluene, m.p. 117–118°, was isolated by conventional methods and weighed 19 g. (54%).

2,6-Dinitrochlorobenzene was prepared by the intriguing method of Borsche and Rantscheff[28b]; it had m.p. 88–89°.

1,4-Dichloro-2,6-dinitrobenzene was prepared by treating 4-chloro-2,6-dinitrophenol with phosphorus oxychloride and diethylaniline[23]; the product had m.p. 104.5–105°.[29]

4-Chloro-3,5-dinitroanisole.—3-Nitro-4-aminoanisole[30a] was nitrated[30b] and the resulting 3,5-dinitro-4-aminoanisole was subjected to the Sandmeyer reaction. The crude 4-chloro-3,5-dinitroanisole was purified by repeated crystallization from dilute acetone, using Norite; eventually, white crystals of m.p. 124–125° were obtained.[31]

3-Nitro-4-chlorobenzotrifluoride.—A sample generously donated by the Hooker Electrochemical Co. was redistilled; a middle fraction of b.p. 110–111° (12 mm.) and n^{24}_D 1.4889 was used in our rate studies.

4-Chloro-3-nitroazobenzene was prepared by the method of Borsche and Exss,[12] whose product melted at 84°. We obtained orange crystals, m.p. 89–89.5°, by crystallization of the crude product from petroleum ether and then from acetic acid slightly diluted with water.

Anal. Calcd. for $C_{12}H_8ClN_3O_2$: C, 55.08; H, 3.08. Found[26]: C, 55.31; H, 3.09.

Methanol.—Reagent grade methanol was dried by the magnesium[32] or aluminum amalgam[33] method. This purified methanol was the solvent for all rate studies, and was also used for preparation of the sodium methoxide reagent.

Comparison of Methoxide Consumption *vs.* Chloride Release.—Samples of all compounds of structure I or II were allowed to react with measured quantities of methanolic sodium methoxide under the conditions to be used in rate studies and long enough to give a large fraction of reaction. Each reaction mixture was titrated with standard sulfuric or perchloric acid to determine the amount of base still remaining, and then halide ion in the titration solution was determined, either gravimetrically or by conductometric or potentiometric titration. From all compounds except II, R = OCH_3, satisfactory checks (within one per cent.) were obtained directly. Two checks on the reaction of 4-chloro-3,5-dinitroanisole (II, R = OCH_3) showed chloride release low by 1.4 and 4.6%.

Product Identification.—The expected products of substitution (anisole derivatives) were isolated from the reactions of all compounds of structure I or II with sodium methoxide under the conditions used for rate studies. The following products were identified.

3-Nitro-4-methoxybenzotrifluoride, m.p. 47–49°[34]; the absence of fluoride ion as a product was established by qualitative tests.

3-Nitro-4-methoxyazobenzene, m.p. 104–105° (lit.[12] 107°).

3,5-Dinitro-4-methoxybiphenyl, m.p. 141–142° (lit.[35] 137–138°).

Anal. Calcd. for $C_{13}H_{10}N_2O_5$: C, 56.93; H, 3.68. Found[36]: C, 57.20; H, 3.68.

2,6-Dinitro-4-methylanisole, m.p. 123–124° (lit.[37] 123°).

2,6-Dinitroanisole, m.p. 117–119°.

4-Chloro-2,6-dinitroanisole, m.p. 64–65° (lit,[38] 66°).

1,4-Dimethoxy-2,6-dinitrobenzene, m.p. 109–111° (lit.[39] 112°).

Rate Measurements.—The procedures of Bunnett, Draper, Ryason, Noble, Tonkyn and Zahler[4] were followed, with some modification, as now noted. The carefully prepared reaction solution, containing arylchloride and methoxide in methanol solution, was placed in a pipetting device and aliquots were dispensed into nitrogen-filled tubes. In the case of runs at 45° or higher, the tubes were sealed, placed in the thermostat all at once, removed at measured times and immediately thrust into a cold bath to effectively stop reaction. Within a few minutes the tubes were opened and their contents transferred quantitatively into beakers containing a measured excess of standard sulfuric acid. In the case of runs at 25° or lower, aliquots of the reaction solution were dispensed into test-tubes which were then tightly capped with rubber stoppers. In such runs, reaction was stopped by pipetting a measured excess of standard sulfuric acid directly into the aliquot of reacting solution. Appropriate corrections were made for thermal expansion or contraction of the solvent. Thermostats were constant to ±0.02°. All thermometers were checked against thermometers certified by the Bureau of Standards.

Reactions were in general followed to about 50% completion, though occasionally as little as 25% or as much as 75% reaction was the basis of study. There was no tendency toward curvature (except in the case of II, R = OCH_3) and relatively little scatter in the plots of $1/(a - x)$ *vs.* t. All rate coefficients were derived from the data by the method of least squares with each point weighted according to the fourth power of the per cent. of aryl chloride unreacted. An average deviation of one per cent. or less between two or more identical runs was our standard of acceptability of measurements, though in a few cases somewhat less precision was accepted, as follows: for I, R = CF_3, at 25.16°, 3.5%; for II, R = C_6H_6, at 24.95°, 2%; for II, R = OCH_3, at 55.20°, 3%; for II, R = Cl, at 25.14°, 2%. In two cases, supposedly identical determinations were made in both the Reed and North Carolina laboratories; the coefficients obtained agreed within an average deviation of one per cent.

In the following list, the rate coefficient from each run is given in units of l. mole^{-1} min.$^{-1}$; coefficients for each compound are given in their chronological order of determination.

Reactions of Structure I with Sodium Methoxide.—R = NO_2, 1.498 and 1.486 at 25.19°.

R = CF_3, 0.0787, 0.0791 and 0.0791 at 44.84°; 0.00995, 0.00902, 0.00896, 0.00966 and 0.00930 at 25.16°.

R = $C_6H_5N_2$, 0.0399 and 0.0407 at 44.90°; 0.1020, 0.1050, 0.1027 and 0.1047 at 55.17°.

Reactions of Structure II with Sodium Methoxide.—R = Cl, 0.0258 and 0.0255 at 0°; 0.360, 0.370, 0.384 and 0.377 at 25.14°.

R = C_6H_5, 0.0673, 0.0643 and 0.0644 at 24.95°; 0.458 and 0.450 at 44.84°.

R = H, 0.0431 and 0.0427 at 24.94°; 0.291, 0.291 and 0.289 at 44.92°.

R = CH_3, 0.0452, 0.0462, 0.0465 and 0.0464 at 45.46°; 0.118 and 0.117 at 55.17°.

R = OCH_3, 0.0111, 0.0120, 0.0144 and 0.0115 at 55.20°; 0.0459 and 0.0467 at 68.84°. Plots of $1/(a - x)$ *vs.* t showed considerable scatter and some downward curvature at 55.20° and marked downward curvature at 68.84°. Therefore it was deemed better to take the initial slope of a composite plot for the four runs at 55.20°, and initial slopes for the runs at 68.84°, as follows: 0.0132 at 55.20°; 0.0527 and 0.0528 at 68.84°.

Acknowledgments.—We thank Mr. William F. Dunn, Jr., for carrying out important preliminary experiments, and Messrs. George T. Davis and William Q. Beard for technical assistance.

Chapel Hill, N. C.

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(29) E. Misslin, *Helv. Chim. Acta*, **3**, 631 (1920), reported m.p. 106°.

(30) (a) Generously donated by E. I. du Pont de Nemours and Co., Inc.; (b) R. C. Elderfield, W. J. Gensler and O. Birstein, *J. Org. Chem.*, **11**, 812 (1946).

(31) H. H. Hodgson and J. H. Crook, *J. Chem. Soc.*, 825 (1933), reported yellow plates, m.p. 123°.

(32) L. F. Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., Boston, Mass., 1941, p. 360.

(33) H. Hartley and H. R. Raikes, *J. Chem. Soc.*, **127**, 524 (1925).

(34) J. H. Brown, C. W. Suckling and W. B. Whalley, *ibid.*, S95 (1949), reported m.p. 48°.

(35) F. Bell and J. Kenyon, *ibid.*, 3048 (1926),

(36) Analysis by Micro-Tech. Laboratories, Skokie, Ill.

(37) W. Borsche, *Ber.*, **56**, 1488 (1923),

(38) A. F. Holleman, *Rec, trav. chim.*, **39**, 435 (1920).

(39) B. Reichert and W. Turkewitsch, *Arch. Pharm.*, **276**, 397 (1938).