122. *Nucleophilic Displacement Reactions in Aromatic Systems. Part VI.* Influence of Nuclear Alkyl Groups in the Aromatic System. Kinetics of the Reactions of Chlorodinitrotoluenes and Related Compounds with Piperidine, Aniline, and Ethoxide Ions in Ethanol, and with Methoxide Ions in Methanol.*

By B. Capon and N. B. Chapman.

Arrhenius parameters are presented for the reactions in ethanol (for amines) or methanol of 1-chloro-2 : 4-dinitrobenzene with piperidine, of 2-chloro-3 : 5-dinitrotoluene with piperidine and with aniline, of 5-chloro-2 : 4-dinitrotoluene with piperidine, aniline, and methoxide ion, and of 3-chloro-2 : 6-dinitrotoluene with piperidine and methoxide ion. Arrhenius parameters are also presented for the reactions in ethanol of 4-*tert.*-butyl-6-chloropyrimidine, of 1-*tert.*-butyl-5-chloro-2 : 4-dinitro- and 1-*tert.*-butyl-3-3-chloro-4-nitro-benzene, of 3-chloro-4-nitro- and 5-chloro-2-nitro-toluene with piperidine, and of the last two compounds with methanolic methoxide. Light-absorption data for six of these compounds and some closely related compounds are also reported.

It is concluded that the polar effect of alkyl groups *meta* to the seat of substitution is predominantly inductive. Evidence is also provided of the primary steric effect of a methyl group *ortho* to the seat of substitution. It is also shown that a methyl or *tert.*-butyl group *meta* to the seat of substitution but *ortho* to an activating nitro-group may exert a secondary steric effect which is powerfully deactivating, especially in the case of 3-chloro-2 : 6-dinitrotoluene. The relevance of the light-absorption results to this phenomenon is discussed, and the relative importance of the secondary steric effect to light absorption and to reaction kinetics is tentatively explained.

This investigation originated from observations by Lindemann and Pabst [1] on the reactivities of chlorodinitrotoluenes towards aniline, and in particular of 3-chloro-2 : 6-dinitrotoluene which was said to be virtually inert. For a fuller elucidation of these phenomena, the reactions of 5-chloro-2 : 4-, 3-chloro-2 : 6-, and 2-chloro-3 : 5-dinitrotoluene with piperidine and with aniline in ethanol and with methanolic methoxide ion have been studied. Since the low reactivity was considered to be due to a secondary steric effect,[2] 1-*tert.*-butyl-5-chloro-2 : 4-dinitrobenzene, in the reactions of which an effect of this kind would be expected to be important, was synthesised and its reactions studied,

* Part V, *J.*, 1956, 1563.

[1] Lindemann and Pabst, *Annalen*, 1928, **462**, 24.
[2] Ingold, " Structure and Mechanism in Organic Chemistry," Bell, London, 1953, pp. 104, 402.

together with those of 5-chloro-2-nitrotoluene for further comparison. A preliminary account of this work has already been given.[3]

It has been suggested [4,5] that the polar deactivating influence of alkyl groups *meta* to the seat of nucleophilic substitution in aromatic systems might be due mainly either to an inductive or a hyperconjugative effect. To attempt to determine which of these effects was the more important, 4-*tert.*-butyl-6-chloropyrimidine and 1-*tert.*-butyl-3-chloro-4-nitrobenzene were synthesised, and the rates and parameters of their reactions were compared with those of 4-chloro-6-methylpyrimidine and of 3-chloro-4-nitrotoluene. Related phenomena have been studied kinetically by Berliner and Monack,[6] Bevan, Hughes, and Ingold,[7] Spitzer and Wheland,[8] and Miller and Williams.[9] A semi-quantitative study has been reported by Anderson, Campbell, and Gilmore.[10]

In addition, the ultraviolet absorption spectra of the chloronitro-compounds mentioned above and those of *m*-dinitrobenzene, 2 : 4-dinitrotoluene, 1-*tert.*-butyl-2 : 4- and 1-chloro-2 : 6-dinitrobenzene, and *p*-chloronitrobenzene have been studied, with a view to discovering roughly the extent of conjugation of nitro-groups with the benzene ring when hindered by *ortho*-substituents. This gives important information about the initial states for many of the reactions studied.

Experimental

Materials.—Chloro-compounds. Chloro-2 : 4-dinitrobenzene, purified as in Part I,[11] had m. p. 50·5°. 5-Chloro-2 : 4-dinitrotoluene was prepared by Reverdin and Crépieux's method [12] and had m. p. 90°. 2-Chloro-3 : 5-dinitrotoluene was prepared by Morgan and Drew's method [13] and recrystallised from ethanol to constant m. p. 61·5° (Morgan and Drew [13] give m. p. 64°). In our hands Körner and Contardi's method [14] for the preparation of 3-chloro-2 : 6-dinitrotoluene proved unsuccessful, and this compound was prepared by nitrating *m*-chlorotoluene (200 g.) by Reverdin and Crépieux's method.[12] Recrystallisation of the product from ethanol (1 l.) gave 5-chloro-2 : 4-dinitrotoluene as major product. The mother-liquor was boiled for 2 hr. with an excess of aniline to remove this compound, and the product was cooled, filtered, and poured on ice and hydrochloric acid, and crude 3-chloro-2 : 6-dinitrotoluene was filtered off. This was distilled at 10^{-3} mm. and crystallised from ethanol to constant m. p. 71·5°; yield 10% (Körner and Contardi [14] give m. p. 73°, cf. Brady and Bowman [14a]).

1-tert.-*Butyl-5-chloro-2 : 4-dinitrobenzene.* To a solution of *p*-acetamido-*tert.*-butylbenzene (56 g.), prepared in 58% yield and of m. p. 168—170° by Carpenter, Easter, and Wood's method,[15] in glacial acetic acid (85 ml.) and concentrated hydrochloric acid (130 ml.) at 0°, was added with stirring at 0—5° a solution of sodium chlorate (15 g., 0·5 mol.) in water (40 ml.), and the mixture was stored for 30 min. at room temperature. Concentrated hydrochloric acid (85 ml.) was then added, and the mixture boiled under reflux for 2 hr. Steam-distillation of the product until 1 l. of liquid had distilled removed most of the acetic acid, and after cooling and alkalinification with concentrated sodium hydroxide solution, further steam-distillation gave 4-tert.-*butyl-2-chloroaniline*, which was extracted with ether, dried (KOH) and after removal of ether was distilled, b. p. 134—143°/15 mm., yield 66% (Found : C, 65·0; H, 7·4; N, 7·1; Cl, 19·2. $C_{10}H_{14}NCl$ requires C, 65·4; H, 7·6; N, 7·6; Cl, 19·3%). Acetylation and recrystallisation from aqueous methanol gave the *acetyl* derivative, m. p. 152·5—153° (Found : C, 64·2;

[3] Capon and Chapman, *Chem. and Ind.*, 1955, 683.
[4] Rees, Thesis, London, 1953.
[5] Brieux and Deulofeu, *J.*, 1954, 2519.
[6] Berliner and Monack, *J. Amer. Chem. Soc.*, 1952, **74**, 1578.
[7] Bevan, Hughes, and Ingold, *Nature*, 1953, **171**, 301.
[8] Spitzer and Wheland, *J. Amer. Chem. Soc.*, 1940, **62**, 2995.
[9] Miller and Williams, *J.*, 1953, 1475.
[10] Anderson, Campbell, and Gilmore, *J.*, 1940, 446.
[11] Bishop, Cavell, and Chapman, *J.*, 1952, 437.
[12] Reverdin and Crépieux, *Ber.*, 1900, **33**, 2506.
[13] Morgan and Drew, *J.*, 1920, **117**, 784.
[14] Körner and Contardi, *Gazzetta*, 1917, **47**, 228.
[14a] Brady and Bowman, *J.*, 1921, **119**, 896.
[15] Carpenter, Easter, and Wood, *J. Org. Chem.*, 1951, **16**, 608.

H, 7·1; N, 6·2; Cl, 15·7. $C_{12}H_{16}ONCl$ requires C, 63·8; H, 7·2; N, 6·2; Cl, 15·7%). Diazotisation of the above base (18·3 g.), dissolved in concentrated hydrochloric acid (40 ml.) and water (15 ml.), with sodium nitrite (7·25 g., 1·05 mol., in 17 ml. of water), followed by treatment during 30 min. with ice-cold 30% (w/w) aqueous hypophosphorous acid (250 ml.) at −5° to 0°, and stirring at 0° for 1 hr., then storage in the refrigerator for 48 hr. gave an oil, which was extracted with ether, and dried ($CaCl_2$), and after removal of ether *m-tert.*-butyl-chlorobenzene was distilled, b. p. 90—95°/15 mm., yield 71%. Deamination of the diazonium salt obtained as above with aqueous ethanol and sulphuric acid in the presence of copper bronze gave only a 22% yield of the required compound. *m-tert.*-Butylchlorobenzene (7·5 g., 0·045 mol.) was added to concentrated sulphuric acid (20 g.) and nitric acid (*d* 1·50, 25 g., 0·4 mol.) at 0—5°. The mixture was shaken at room temperature for 8 hr. and heated at 40° for 36 hr., then poured on ice. The resulting solid (12 g.) was filtered off and recrystallised from ethanol to give 1-tert.-*butyl*-5-*chloro*-2 : 4-*dinitrobenzene*, m. p. 94·5—95·0°, yield 30% (Found: C, 46·8; H, 4·2; N, 9·8; Cl, 13·6. $C_{10}H_{11}O_4N_2Cl$ requires C, 46·4; H, 4·3; N, 10·8; Cl, 13·7%). The colourless product turns yellow on exposure to light and should be stored in the dark.

Chloronitrotoluenes. Nitration of *m*-toluidine in acetic anhydride by Coffey's method [16] gave 4-nitroaceto-*m*-toluidide, which on hydrolysis with hydrochloric acid, diazotisation, and treatment with cuprous chloride in hydrochloric acid gave 3-chloro-4-nitrotoluene, m. p. 25—26°, after crystallisation from light petroleum (b. p. 40—60°). 5-Chloro-2-nitrotoluene was prepared from 6-nitroaceto-*m*-toluidide, prepared by McGookin and Swift's method,[17] by a method similar to that used for converting 4-nitroaceto-*m*-toluidide into 3-chloro-4-nitrotoluene, and after crystallisation from light petroleum (b. p. 40—60°) had m. p. 24—24·5°, b. p. 130—135°/20 mm.

1-tert.-*Butyl*-3-*chloro*-4-*nitrobenzene*. *m-tert.*-Butylaniline (44 g., 0·30 mol.), prepared by Carpenter, Easter, and Wood's method,[15] was dissolved in acetic anhydride (150 ml.) and pure cupric nitrate trihydrate (34·4 g., 0·14 mol.) was added to the stirred solution at 0° during 30 min. The mixture was stirred for a further 60 min. at 0° and kept at room temperature for 12 hr., then poured into ice-water (3 l.) and stirred for 12 hr. completely to hydrolyse the acetic anhydride. 3-Acetamido-1-*tert.*-butyl-4-nitrobenzene was filtered off and recrystallised from aqueous methanol; it had m. p. 116—117°, yield 58%. This (37 g., 0·15 mol.) was boiled under reflux with concentrated hydrochloric acid (146 ml.) and water (61 ml.) for 12 hr., and the resultant solution was cooled to 0° and sodium nitrite (11·4 g., 0·165 mol.) in water (25 ml.) was gradually added at ~5°. The diazonium solution was added slowly to a solution of cuprous chloride (15 g.) in concentrated hydrochloric acid (200 ml.) at 60°. The mixture was heated at ~100° for 30 min. and the resultant oil was steam-distilled, dried ($CaSO_4$), and distilled to give 1-tert.-*butyl*-3-*chloro*-4-*nitrobenzene*, b. p. 90—95°/0·015 mm., n_D^{18} 1·5442 (Found: C, 55·8; H, 5·3; N, 6·1; Cl, 16·4. $C_{10}H_{12}O_2NCl$ requires C, 56·2; H, 5·6; N, 6·6; Cl, 16·4%).

4-tert.-*Butyl*-6-*chloropyrimidine*. Ethyl 3 : 3-dimethyl-2-oxo-butane-1-carboxylate, prepared by Levine and Hauser's method,[18] was condensed with thiourea by Anderson, Halverstadt, Miller, and Roblin's method [19] to give 6-*tert.*-butyl-2-thiouracil, which on desulphurisation with Raney nickel [20] gave 4-tert.-*butyl*-6-*hydroxypyrimidine*, crude yield 97%, m. p. 217·5—218·5° after recrystallisation from ethanol (Found: C, 62·9; H, 8·0; N, 17·9. $C_8H_{12}ON_2$ requires C, 63·1; H, 8·0; N, 18·4%). The crude product (5 g.) was heated with phosphoryl chloride (58 g.) on a boiling-water bath for 2 hr., two-thirds of the unchanged phosphoryl chloride was removed at 20 mm., and the residue was poured into ice-water covered with a layer of ether. The mixture was neutralised (pH 7) with sodium hydroxide, and the ethereal layer was separated. The aqueous layer was further extracted with ether and the combined extracts were dried ($CaSO_4$). The ether was removed under reduced pressure and the resulting white solid was sublimed at 30°/15 mm. to give 4-tert.-*butyl*-6-*chloropyrimidine*, m. p. 38·5—39·0°, yield 53% (Found: C, 56·2; H, 6·8; N, 16·2; Cl, 20·8. $C_8H_{11}N_2Cl$ requires C, 56·4; H, 6·5; N, 16·4; Cl, 20·8%). *p*-Chloronitrobenzene was purified as described in Part IV,[21] and had m. p. 83°. 1-Chloro-2 : 6-dinitrobenzene was prepared by Welsh's method [22] and had m. p. 86—87°.

[16] Coffey, *J.*, 1926, 3219.
[17] McGookin and Swift, *J. Soc. Chem. Ind.*, 1939, **58**, 152.
[18] Levine and Hauser, *J. Amer. Chem. Soc.*, 1944, **66**, 1768.
[19] Anderson, Halverstadt, Miller, and Roblin, *ibid.*, 1945, **67**, 2197.
[20] Brown, *J. Soc. Chem. Ind.*, 1950, **69**, 353.
[21] Chapman, Parker, and Soanes, *J.*, 1954, 2109.
[22] Welsh, *J. Amer. Chem. Soc.*, 1941, **63**, 3277.

1-*tert.*-Butyl-2 : 4-dinitrobenzene was prepared by Wepster and his co-workers' method [23] and crystallised from ethanol to a constant m. p. of 61—62°. The colourless product turned yellow on exposure to light and was stored in the dark. *m*-Dinitrobenzene (from British Drug Houses Ltd.) was recrystallised from ethanol to a constant m. p. of 89·0°. 2 : 4-Dinitrotoluene (from British Drug Houses Ltd.) was similarly recrystallised and had m. p. 70·5—71·0°.

Amines. Aniline was purified as described in Part I [11] and piperidine as described in Part III.[24]

Solvents.—99·8% Ethanol was prepared as described in Part I,[11] and methanol was dried by Lund and Bjerrum's method [25] and redistilled, the first 500 ml. of each 4 l. batch being rejected. It had b. p. 64·7°/760 mm.

Reaction Products.—These were isolated from solutions used in kinetic experiments, and save for the new compounds mentioned below, were characterised by their m. p.s. The piperidino- and anilino-derivatives were obtained by distilling off the ethanol, adding water to the product, and filtering off the solid produced. The methoxy-compound was obtained by pouring the reaction mixture into ice-water and filtering off the solid produced.

2 : 6-*Dinitro*-3-*piperidinotoluene*, light yellow needles from ethanol, had m. p. 55·0—55·6° (Found : C, 54·7; H, 5·9; N, 16·0. $C_{12}H_{15}O_4N_3$ requires C, 54·3; H, 5·7; N, 15·9%). 3 : 5-*Dinitro*-2-*piperidinotoluene*, orange needles from methanol, had m. p. 88—89° (Found : C, 53·8; H, 5·8; N, 15·6%). 1-tert.-*Butyl*-2 : 4-*dinitro*-5-*piperidinobenzene*, orange plates from methanol, had m. p. 128—129° (Found : C, 58·7; H, 6·8; N, 13·2. $C_{15}H_{22}O_4N_2$ requires C, 58·6; H, 6·8; N, 13·7%). 4-tert.-*Butyl*-6-*piperidinopyrimidine*, colourless needles from ice-cold methanol, had m. p. 71—72° (Found : C, 70·5; H, 9·2; N, 19·7. $C_{13}H_{21}N_3$ requires C, 71·2; H, 9·6; N, 19·2%). 4-*Nitro*-3-*piperidinotoluene*, orange needles from methanol at −78°, had m. p. 34—35° (Found : C, 65·0; H, 7·2; N, 12·9. $C_{12}H_{16}O_2N_2$ requires C, 65·5; H, 7·3; N, 12·7%). 1-tert.-*Butyl*-4-*nitro*-3-*piperidinobenzene*, a red solid from methanol at −78°, had m. p. 46—46·5° (Found : C, 68·5; H, 8·5; N, 9·7. $C_{15}H_{22}O_2N_2$ requires C, 68·7; H, 8·4; N, 10·7%). 3-*Methoxy*-2 : 6-*dinitrotoluene*, colourless needles from methanol, had m. p. 116—117° (Found : C, 45·7; H, 3·9; N, 13·3. $C_8H_8O_5N_2$ requires C, 45·3; H, 3·8; N, 13·2%); this compound had been prepared by Drew,[26] but was incompletely analysed, and had m. p. 115°.

Procedure.—This was as described in Part V.[27] For all experiments the method of sealed bulbs was used, save for reactions with amines lasting less than 12 hr. at or below 40°. Sodium methoxide solutions were prepared by dissolving clean sodium in pure methanol. Carbonate content was found to be negligible. Chloride-ion determinations after about 30 times the " half-life " of the reaction always corresponded to 99·5—100·5% reaction, thus checking the purity of the chloro-compounds and indicating the absence of reversibility.

Light-absorption Measurements.—A Hilger " Uvispek " instrument was used, with quartz cells 0·5 cm. long. Solutions were chosen of such concentration that the optical densities at the maxima were in the range 0·5—1·8.

Results are assembled in Table 4.

Results

Detailed values for some of the reactions are given in Table 1 and all the results are summarised in Table 2. In view of previous verification of order of reaction for very similar reactions, and of the self-consistent second-order coefficients obtained, no order determinations were carried out. Experimentally observed times are recorded in sec., min., or hours, but the velocity coefficients are given in l. mole^{-1} sec.$^{-1}$. Errors in k given after the ± sign are mean deviations from the mean. Temperatures in the range 20—90° are accurate to ±0·03°, and in the range 90—160° to ±0·12° or better. The rate laws quoted in Part V [27] are applicable, and a is the initial concentration of the reagent, and b that of the chloro-compound. All reactions were carried out in 99·8% ethanol, save those of the methoxide ion which were done in pure methanol.

[23] Biekart, Dessens, Verkade, and Wepster, *Rec. Trav. chim.*, 1952 **71**, 321.
[24] Chapman and Rees, *J.*, 1954, 1190.
[25] Lund and Bjerrum, *Ber.*, 1931, **64**, 210.
[26] Drew, *J.*, 1920, **117**, 1618.
[27] Chapman and Russell-Hill, *J.*, 1956, 1563.

TABLE 1.

Reactions of aniline

3-*Chloro*-2 : 6-*dinitrotoluene at* 145·0°. a = 0·2167M, b = 0·0500M.

Time (hr.)	7·00	15·00	24·00	39·00	63·00	144·00
Decompn. (%)	11·3	15·2	21·3	29·2	39·6	51·8
10^5k	2·25	1·46	1·35	1·22	1·14	1·04

2-*Chloro*-3 : 5-*dinitrotoluene at* 60·0°. a = 0·2424M, b = 0·04946M.

Time (hr.)	3·00	8·00	15·00	26·00	29·00	36·00	47·00	72·00	96·00
Decompn. (%)	5·8	14·5	25·2	38·2	41·4	48·5	56·8	69·3	77·9
10^5k	2·31	2·32	2·34	2·33	2·34	2·38	2·37	2·32	2·28

Mean $k = 2·33 \pm 0·02 \times 10^{-5}$; after correction for solvent expansion, $k = 2·46 \pm 0·02 \times 10^{-5}$

Reactions of piperidine.

5-*Chloro*-2 : 4-*dinitrotoluene at* 30·0°. a = 0·1996M, b = 0·03864M.

Time (sec.)	120	247	485	600	720	840	960	1080
Decompn. (%)	17·5	32·4	52·0	58·9	68·8	70·4	74·8	78·5
10^3k	(8·34)	8·53	8·57	8·58	8·86	8·52	8·81	8·89

Mean $k = 8·68 \pm 0·15 \times 10^{-3}$.

4-tert.-*Butyl*-6-*chloropyrimidine at* 40·0°. a = 0·1698M, b = 0·03954M.

Time (min.)	10·0	20·0	35·0	50·0	70·0	90·0	110·0	140·0
Decompn. (%)	13·6	24·2	32·2	48·8	59·9	67·7	73·6	79·3
10^3k	1·48	1·44	1·44	1·51	1·54	1·54	1·52	1·52

Mean $k = 1·50 \pm 0·03 \times 10^{-3}$.

5-*Chloro*-2-*nitrotoluene at* 130·0°. a = 0·2037M, b = 0·04790M.

Time (hr.)	8·00	24·2	34·0	44·2	58·0	67·8	103·0
Decompn. (%)	13·1	33·3	42·5	50·5	59·2	64·6	77·8
10^5k	(2·46)	2·49	2·50	2·52	2·52	2·57	2·61

Mean $k = 2·53 \pm 0·03 \times 10^{-5}$; after correction for solvent expansion, $k = 2·96 \pm 0·04 \times 10^{-5}$.

Reactions with sodium methoxide.

3-*Chloro*-4-*nitrotoluene at* 80·0°. a = 0·1171M, b = 0·05329M.

Time (hr.)	6·00	12·10	18·20	24·60	32·00	40·00	50·00	63·10	97·00
Decompn. (%)	10·0	19·3	26·8	33·8	40·6	47·0	53·8	61·2	73·9
10^5k	4·31	4·40	4·36	4·34	4·32	4·29	4·28	4·29	(4·20)

Mean $k = 4·32 \pm 0·03 \times 10^{-5}$; after correction for solvent expansion, $k = 4·67 \pm 0·03 \times 10^{-5}$.

5-*Chloro*-2-*nitrotoluene at* 90·0°. a = 0·1167M, b = 0·04764M.

Time (hr.)	4·00	6·00	9·00	12·00	16·00	22·00	25·00	40·20
Decompn. (%)	17·8	24·9	34·3	42·7	51·5	62·3	65·8	79·8
10^4k	1·21	1·20	1·20	1·22	1·21	1·25	1·22	1·21

Mean $k = 1·22 \pm 0·01 \times 10^{-4}$; after correction for solvent expansion, $k = 1·34 \pm 0·01 \times 10^{-4}$.

TABLE 2.

	Piperidine			Aniline		
Chloro-compound	20·0° (i)	30·0° (i)	40·0° (i)	40·0° (ii)	50·0° (ii)	60·0° (ii)
1-Chloro-2 : 4-dinitrobenzene	158—168	308—315	512—543	—	—	—
5-Chloro-2 : 4-dinitrotoluene	44·3—46·0	83·4—88·9	155—167	47·2—49·0	81·6—85·5	140—148
3-Chloro-2 : 6-dinitrotoluene	0·166—0·173	0·383—0·397	0·857—0·877	—	—	—
2-Chloro-3 : 5-dinitrotoluene	0·581—0·606	1·28—1·35	2·81—2·92	7·19—7·37	13·4—13·8	23·9—25·0
1-*tert.*-Butyl-5-chloro-2 : 4-dinitrobenzene	2·68—2·88	5·67—6·00	11·5—12·0	—	—	—
4-*tert.*-Butyl-6-chloropyrimidine	4·45—4·47	8·13—8·40	14·4—15·4	—	—	—
	90·0°	100·0°	110·0°			
3-Chloro-4-nitrotoluene	0·300—0·315	0·580—0·601	1·08—1·15	—	—	—
1-*tert.*-Butyl-3-chloro-4-nitrobenzene	0·223—0·230	0·426—0·451	0·812—0·862	—	—	—
	130·0°	143·8°	161·7°			
5-Chloro-2-nitrotoluene	0·288—0·305	0·577—0·677	1·09—1·14	—	—	—

TABLE 2. (*Continued.*)

	Methoxide ion			Ethoxide ion
	20·0° (i)	30·0° (i)	40·0° (i)	20·0° (i)
3-Chloro-2 : 6-dinitrotoluene	0·525—0·564	1·60—1·73	4·75—5·09	1·00—1·04
2-Chloro-3 : 5-dinitrotoluene	—	—	—	26·3—28·2
5-Chloro-2 : 4-dinitrotoluene	41·3—42·1	114—117	287—299	—
5-Chloro-2-nitrotoluene * ...	0·498—0·534	1·31—1·37	3·28—3·38	—
3-Chloro-4-nitrotoluene † ...	0·163—0·170	0·462—0·475	1·19—1·22	—

(i) Extreme values of 10^4k in l. mole^{-1} sec.$^{-1}$ for a given experiment. (ii) Similarly for 10^6k. Not less than 70% of the reaction was usually studied. (For mean k's at 30·0°, see Table 3.)
* 60° higher. † 50° higher.

TABLE 3.

	Piperidine at 30°			Methoxide ion at 30°			Aniline at 40°	
Chloro-compound	10^4k	E (cal./mole)	$\log_{10}A$	10^4k	E (cal./mole)	$\log_{10}A$	10^5k	E (cal./mole)	$\log_{10}A$
Chloro-2 : 4-dinitrobenzene	309	10,700	6·2	—	—	—	—	—	—
5-Chloro-2 : 4-dinitrotoluene	86·7	11,600	6·3	116	17,700	10·8	4·82	11,100	3·5
3-Chloro-2 : 6-dinitrotoluene *	0·391	14,900	6·3	1·68	20,500	11·0	0·728	12,600	3·6
2-Chloro-3 : 5-dinitrotoluene *	1·32	14,500	6·6	—	—	—	—	—	—
1-*tert.*-Butyl-5-chloro-2 : 4-dinitrobenzene	5·85	13,000	6·2	—	—	—	—	—	—
4-*tert.*-Butyl-6-chloropyrimidine	8·33	11,000	4·9	—	—	—	—	—	—
5-Chloro-2-nitrotoluene	0·296 ‡	22,900	7·7	1·34 †	24,500	10·9	—	—	—
3-Chloro-4-nitrotoluene	0·303 †	17,800	6·2	1·20 †	24,700	10·9	—	—	—
1-*tert.*-Butyl-3-chloro-4-nitrobenzene	0·228 †	18,000	6·2	—	—	—	—	—	—

Units of A and k are l. mole^{-1} sec.$^{-1}$. Energies of activation are accurate to ± 300 cal./mole. The values of k are mean values from independent determinations and are accurate to ± 2% or better.
† At 90°. ‡ At 130°.
* For reaction with ethanolic ethoxide ion at 20°, 10^4k = 1·02 and 26·5 respectively.

TABLE 4.

Compound	$\lambda_{max.}$ (Å)	$10^{-3}\varepsilon_{max.}$ (l. mole^{-1} cm.$^{-1}$)
m-Dinitrobenzene *	2330—2350	17·4
2 : 4-Dinitrotoluene *	2420	14·6
1-*tert.*-Butyl-2 : 4-dinitrobenzene	2600	10·7
Chloro-2 : 4-dinitrobenzene	2400	11·9
5-Chloro-2 : 4-dinitrotoluene	2470—2500	14·1
1-*tert.*-Butyl-5-chloro-2 : 4-dinitrobenzene	2440—2500	7·7 (infl.)
3-Chloro-2 : 6-dinitrotoluene	2500—2520	6·9
2-Chloro-3 : 5-dinitrotoluene	2470—2490	10·8
Chloro-2 : 6-dinitrobenzene	No maxima	†
p-Chloronitrobenzene *	2700—2720	10·5
5-Chloro-2-nitrotoluene	2670	7·5

* The results with these compounds agree well with those of previous workers [28] save for the results of Canback.[29]
† $\varepsilon = 8{\cdot}3 \times 10^3$ at 2400 Å.

DISCUSSION

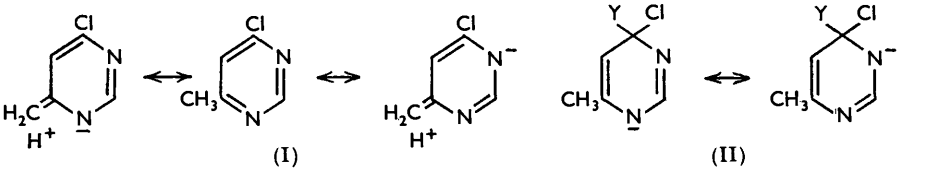
Reaction Mechanism.—Throughout what follows the reaction mechanism discussed in Part V [27] will be assumed to operate, and in particular, a study of the reaction products

[28] (*a*) Kortüm, *Z. phys. Chem.*, 1939, *B*, **42**, 39; (*b*) Fielding and Le Fèvre, *J.*, 1950, 2812; (*c*) Doub and Vanderbelt, *J. Amer. Chem. Soc.*, 1947, **69**, 2714; (*d*) Ungnade, *ibid.*, 1954, **76**, 1601; (*e*) Schroeder, Wilcox, Trueblood, and Dekker, *Analyt. Chem.*, 1951, **23**, 1740.
[29] Canback, *Farm. Rev.*, 1949, **48**, 217.

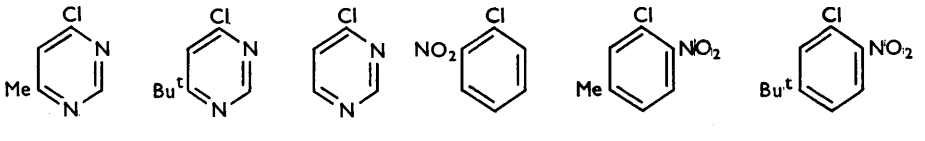
p. 663) shows the absence of *cine*-substitution, and a study of the "t_∞" values absence of reversibility (cf. p. 603).

Polar Effects of meta-*Alkyl Groups.*—In Part III,[24] Chapman and Rees recorded the kinetic influence of a *meta*-methyl substituent on the reactivity of 2- or 4-chloropyrimidine in aromatic nucleophilic substitution. The rate-diminishing influence of the substituent may be ascribed to its electron-releasing inductive effect, or to a hyperconjugative stabilisation of the initial state (I), which is structurally precluded in the transition state if it has mainly structure (II).

The results summarised below for reactions with piperidine lead us to the view that the inductive effect predominates since the hyperconjugative effect (rate-diminishing) of the *meta-tert.*-butyl group should be less, whereas its inductive effect (also rate-diminishing) should be greater than that of a *meta*-methyl group. A similar phenomenon has been discovered by Hughes and his co-workers [30] in electrophilic substitution. It is noteworthy that in the present case the difference in polar effect on reaction rate manifests itself in the log A or entropy term, but its magnitude is too small for further analysis to be



(I) (II)



(III) (IV) (V) (VI) (VII) (VIII)

	(III)	(IV)	(V)
10^4k_{20} (l. mole sec.$^{-1}$)	11·4 *	4·47	~14 *
E (cal. mole^{-1})	11,000 *	11,000	~10,500 *
log A	5·2 *	4·9	~5·0 *

* Ref. 24.

		(VI)	(VII)	(VIII)
Piperidine in ethanol	10^5k_{90} (l. mole^{-1} sec.$^{-1}$)	2·98 *	3·03	2·28
	E (cal. mole^{-1})	18,100 *	17,800	18,000
	log A	6·4 *	6·2	6·2
Methoxide ion in methanol	10^4k_{90} (l. mole^{-1} sec.$^{-1}$)	1·50 †	1·20	—
	E (cal. mole^{-1})	23,500 †	24,700	—
	log A	10·3 †	10·9	—

* Ref. 28. † Ref. 9.

warranted. Brieux and Deulofeu [5] discovered that the effect of a *meta*-methyl group on the reactivity of *o*-chloronitrobenzene towards piperidine in benzene was barely perceptible (rate ratio 1·01 at 100°). Our observations for reactions in ethanol or methanol are summarised in the Chart above, and confirm those of Brieux and Deulofeu for reactions with piperidine. It will be seen that the influence of *meta*-methyl and *-tert.*-butyl groups is mainly in the same sense as that observed for displacements activated by two cyclic nitrogen atoms, but much smaller in magnitude. We regard these results as confirmation of our view as to polar effects of *meta*-alkyl groups.

The Primary Steric Effect.—If an alkyl group occupies a position *ortho* to the seat of substitution, its polar influence on a reaction is, in principle, complicated by its primary steric effect (steric hindrance, cf. ref. 2, p. 100). However, it can be deduced that the polar effect of an *ortho*-alkyl group is unlikely to be large, from the measured mainly hyperconjugative polar effects of *para*-alkyl groups on nucleophilic aromatic substitution.[6,7]

[30] Cohn, Hughes, Jones, and Peeling, *Nature*, 1952, **169**, 291.

These effects often cause a 3—6-fold decrease in rate and increase in E of ~1000 cal. mole^{-1}, depending on conditions. However the effect of the *ortho*-methyl group is much larger, as can be seen from the results in Table 5. This must be ascribed mainly to a primary steric effect of the *ortho*-methyl group, especially as the effect is much more marked with

TABLE 5.*

	Piperidine †			Aniline †			Methanolic methoxide		
	10^4k_{20}	E	log A	10^5k_{40}	E	log A	10^4k_{20}	E	log A
(IX)	163	10,700	6·2	16·2	11,200	4·0 ‡	180	17,400	11·3 §
(X)	0·59	14,500	6·6	0·73	12,600	3·6	13·3	19,200	11·4

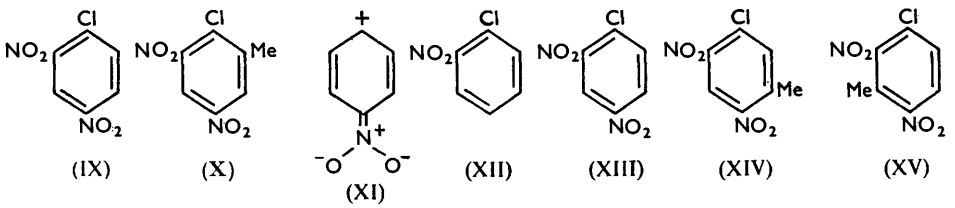
* k in l. mole^{-1} sec.$^{-1}$; E in cal. mole^{-1}. † In 99·8% ethanol. ‡ Ref. 31. § Ref. 9.

TABLE 6.*

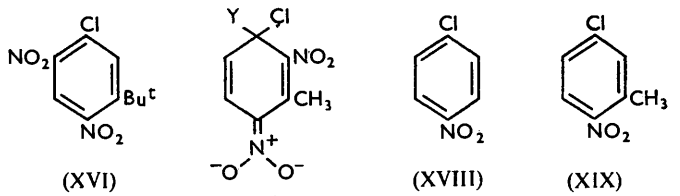
		(XII)	(XIII)	(XIV)	(XV)	(XVI)
Piperidine	10^4k_{20}	8 × 10^{-4} †	163	44·9	0·168	2·82
	E	18,100 §	10,700	11,600	14,900	13,000
	log A	6·4 §	6·2	6·3	6·3	6·2
Methoxide ion	10^4k_{20}	6 × 10^{-4} †	1800 †	41·9	0·530	—
	E	23,500 ‡	17,400 ‡	17,700	20,500	—
	log A	10·3 ‡	11·3 ‡	10·8	11·0	—

* k in l. mole^{-1} sec.$^{-1}$; E in cal. mole^{-1}. † Evaluated from Arrhenius parameters. ‡ Ref. 9. § Ref. 21.

piperidine than with aniline or methoxide ion, a view confirmed by inspection of appropriate models of the various transition states. The main kinetic effect is an increase in E varying from ~4000 to ~1400 cal. mole^{-1}. Cortier, Fierens, Gilon, and Halleux [32] have observed a similar phenomenon in the reactions of the two chloro-compounds included



(IX) (X) (XI) (XII) (XIII) (XIV) (XV)



(XVI) (XVII) (XVIII) (XIX)

in Table 5 with iodide ion in acetone. It is noteworthy that in similar reactions of 1-alkyl-2-bromo-3 : 5-dinitrobenzenes Fierens and Halleux [33] found that the major kinetic influence of varying the alkyl group systematically from methyl through ethyl and *iso*-propyl to *tert.*-butyl was a decrease in log A, by comparison with 1-bromo-2 : 4-dinitrobenzene, accompanied by a decrease in E.

Secondary Steric Effects.—The more pronounced effect of *meta*-methyl substituents in the reactions of 1-chloro-2 : 4-dinitrobenzene derivatives is set out in Table 6. For the reactions with piperidine log A is constant within experimental error, and this is also true for reactions of methoxide ion, with one exception, thus simplifying interpretation of the results, since the relative E values may be regarded as relative potential energies of

[31] Singh and Peacock, *J. Phys. Chem.*, 1936, **40**, 669.
[32] Cortier, Fierens, Gilon, and Halleux, *Bull. Soc. chim. belges*, 1955, **64**, 709.
[33] Fierens and Halleux, *ibid.*, p. 696.

activation. These results are to be understood in terms of the secondary steric effect of *meta*-alkyl groups, the polar influence of the *meta*-alkyl groups being slight (p. 606). Before details are considered it is valuable to examine the light-absorption data in Table 4, which provide information about the probable extent of conjugation of the nitro-groups with the ring in the initial states of the various reactions.

The influence of *ortho*-alkyl groups and of *ortho*-halogen atoms on the light absorption of nitrobenzene has been discussed by Brown and Regan [34] and by Ungnade [28d] respectively, on the basis of a first excited state tending to a planar dipolar structure (XI). Application of a roughly quantitative treatment due to Braude and Sondheimer [35] to these results leads to estimates of the angle (θ) between the plane of the ring and that of the nitro-group in the initial or ground state. These are as follows [θ in parentheses following X in o-$C_6H_4(NO_2)X$]: Me (55°), Pr^i (69°), Bu^t (90°), F (34°), Cl, (69°), Br, (74°), I (81°). Similar values for θ may be expected to arise from the influence of *ortho*-methyl and *-tert.*-butyl groups, and chlorine atoms in *m*-dinitrobenzene.

The introduction of a second substituent into *m*-dinitrobenzene, as in the chlorodinitrotoluenes, further complicates the spectra, but the strong secondary steric effect of a methyl group inserted between the nitro-groups in 1-chloro-2 : 4-dinitrobenzene is clearly indicated by the results for 3-chloro-2 : 6-dinitrotoluene, whereas a weaker effect, which may be due to " buttressing," [36] is probable in 2-chloro-3 : 5-dinitrotoluene when the methyl group is adjacent to the chlorine atom, but a strong effect is expected again with 1-*tert.*-butyl-5-chloro-2 : 4-dinitrobenzene. The results for 5-chloro-2 : 4-dinitrotoluene appear anomalous and no explanation for this is advanced at present, especially as a similarly placed methyl group inserted into *p*-chloronitrobenzene (giving 5-chloro-2-nitrotoluene) causes the expected decrease in intensity of absorption.

The kinetic influence of the secondary steric effect is very clear from the data for the reaction of 3-chloro-2 : 6-dinitrotoluene with piperidine, insertion of the *meta*-methyl group causing a rise in E of ~4200 cal. mole^{-1}. For methoxide ion reactions the rise is ~3100 cal. mole^{-1}. If the structure of the transition state (formula (XVII shows an extreme form in which the conjugation of the nitro-group with the ring is supposed to be maximal, because of a coplanar structure, achieved at the expense of steric compression) lies nearer to that of the reactants for reactions with alkoxide ions than for those with amines, as suggested by Parks *et al.*, [37] then the influence of the secondary steric effect should be less for the former reactions. We suggest that our results support the view of Parks *et al.* Lindemann and Pabst's original observation [1] as to the lack of reactivity of 3-chloro-2 : 6-dinitrotoluene arises from an initial rate for the reaction with aniline at 50° about 10^4 times smaller than that for chloro-2 : 4-dinitrobenzene. It is clear that the transition state for this reaction must be such as to be highly susceptible to the secondary steric effect, *i.e.*, it probably lies very close to the extreme form (XVII). Moreover, the methyl group in 3-chloro-2 : 6-dinitrotoluene is so placed as to exert the maximum steric effect, being " buttressed " [36] by groups on either side which prevent bending of the C–C bond and interact with both activating nitro-groups. Lindemann and Pabst [1] also found 3-chloro-2 : 6-dinitrotoluene to be virtually inert towards boiling ethanolic aniline, but we have observed a displacement of chlorine in the same system at 145°. However, the reaction shows decreasing rate coefficients as it proceeds (Table 1), and this is probably caused by concomitant reduction and consequent decrease of reactivity of the 3-chloro-2 : 6-dinitrotoluene. The same compound also reacts with ethanolic ethoxide ions similarly, but with methanolic methoxide ions regular second-order kinetics are observed (Table 6). For 5-chloro-2 : 4-dinitrotoluene the rate ratio relative to 1-chloro-2 : 4-dinitrobenzene is ~0·5 for reaction with aniline at 50° and ~0·3 for reaction with piperidine

[34] Brown and Regan, *J. Amer. Chem. Soc.*, 1947, **69**, 1032.
[35] Braude and Sondheimer, *J.*, 1955, 3754.
[36] Rieger and Adams, *J. Amer. Chem. Soc.*, 1950, **72**, 19.
[37] Parks, Hammond, and Hawthorne, *ibid.*, 1955, **77**, 2903.

at 40°. Although the light-absorption data for 5-chloro-2 : 4-dinitrotoluene are anomalous, the kinetic influence of a weakened secondary steric effect is observed, especially in reactions with piperidine (cf. Chapman and Rees [24] for an example in the pyridine series). A similar phenomenon was observed when only one nitro-group is activating as shown in Table 7.

TABLE 7.*

	Piperidine			Methoxide ion	
	(XVIII)	(XIX)		(XVIII)	(XIX)
10^5k_{90}	1·1 †	0·08	10^4k_{90}	5·2 §	1·3
E	17,100 †	22,900	E	23,700 §	24,500
log A	5·3 †	7·7	log A	11·0 §	10·9

* k in l. mole^{-1} sec.$^{-1}$; E in cal. mole^{-1}. † Ref. 21. § Ref. 9.

We revert to the influence of the secondary steric effect on light absorption. Brown and Regan [34] showed that the K-band characteristic of conjugation of a nitro-group with the ring is absent from the spectrum of *o-tert.*-butylnitrobenzene. The kinetic influence of a *tert.*-butyl group adjacent to the *para*-nitro-group in 1-chloro-2 : 4-dinitrobenzene is, however, much smaller than that of removal of the *para*-nitro-group altogether, as can be seen from Table 6. The reason for this difference may be as follows, a dipolar planar first excited state being assumed (cf. XI). A compound with a *tert.*-butyl group *ortho* to a nitro-group will have very few molecules in which the nitro-group is coplanar with the benzene ring in the ground state (initial state), since insufficient energy to effect the necessary steric compression will be available at ordinary temperatures. Moreover, according to the Franck–Condon principle, electronic excitation occurs much more rapidly than molecular rotations and vibrations, hence only very few of the molecules in the ground state will have the correct configuration for excitation, even though the energy of compression necessary to attain a planar state may be small compared with the energy of electronic excitation. Alternatively, we may say that there is insufficient time for the nitro-group to become coplanar with the ring despite the fact that the necessary energy may be available. Hence the K-band will not be observed. However, when a molecule such as 1-*tert.*-butyl-5-chloro-2 : 4-dinitrobenzene passes from the initial to the transition state in a chemical reaction, there will be time for the nitro-group to take up the coplanar configuration and the increase in energy of activation will depend on the difference in compression energy between the initial and the transition state, rather than on the increase associated with the complete removal of the conjugative effects of the nitro-group. We may expect that, in general, light absorption will be more sensitive to the secondary steric effect than chemical reaction, a view confirmed broadly by the results discussed above.

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