CCXCIX.—*The Relative Directive Powers of Groups of the Forms* RO *and* RR′N *in Aromatic Substitution. Part VI. The Nitration of* m- *and* p-*Chlorobenzyl Ethers of Guaiacol.*

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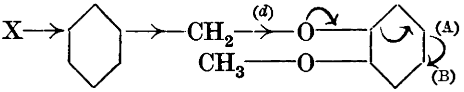
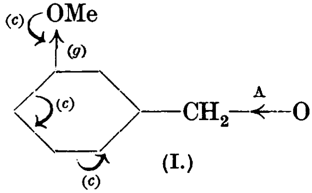
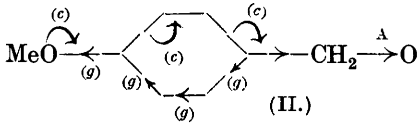
IN studying the relative directive powers of substituted benzyloxy-groups, we examine, in effect, the influence of the modified benzyl group on the electrons of the oxygen atom, and an important feature of the method is that the reactive centres are spatially removed from the benzyl group. The annexed diagram serves to illustrate this point, and just as Flürscheim secured a more just comparison of groups by excluding for certain purposes the ortho-derivatives, so we imagine that the device of relaying the effects of a group and estimating them at a distant point in the molecule constitutes a further step in the same direction.



In the case represented, X and also $X{\cdot}C_6H_4$ are hypothetical kations that have a smaller electron affinity than a proton : this produces an electron displacement (*d*) in the sense indicated and relative to the mean positions of electrons in the corresponding position in the methoxy-group. The contiguous oxygen atom and the associated crotenoid system are thus stimulated, and the velocity of substitution at (B) is greater than that at (A). Groups are compared by putting them separately into competition with methoxyl, and in Part II (J., 1926, 383) it was shown in this way that the directive powers of the *m*-nitrobenzyloxy- and *p*-nitrobenzyloxy-groups are approximately equal (67; MeO = 100). Similarly, the directive power of the *m*-methoxybenzyloxy-group was found to be 92, indicating that in the absence of conjugative disturbances, admittedly never completely eliminated in the formal systems, the methoxyl group must be regarded as one that has a greater electron affinity than hydrogen (I; resultant effect $g>c$ at A). Unfortunately, the directive power of the *p*-methoxybenzyloxy-group could not be determined; we had anticipated a considerably augmented value (>113, the directive power of the benzyloxy-group) as the result of the combined conjugative and general effect shown in (II) ($c>g$ at A).



(I.)



(II.)

The chlorine atom has a greater electron affinity than the methoxyl group, implying an increased general effect and a decreased conjugative effect, and the theoretical disparity between the directive powers of *m*- and *p*-chlorobenzyloxy-groups is thus smaller than that which should exist between the directive powers of the *m*- and *p*-methoxybenzyloxy-groups. Actually, we find that *m*-chlorobenzyloxy- has the directive power 69, and *p*-chlorobenzyloxy- 82. In both cases, therefore, the general effect of chlorine is paramount, but the higher value for the para-derivative is in harmony with our theoretical anticipations, and is probably due to crotenoid conjugation analogous to that symbolised in (II). The close approach of the directive power of *m*-chlorobenzyloxy- to that of *m*-nitrobenzyloxy-, showing that the electron affinity of chlorine is almost as strong as that of the nitro-group, need not occasion surprise, since the charges in the semi-polar double bonds, often assumed to be integral, are not really effective as such on account of the distortion and polarisation of the atoms that must enfeeble their external fields. It is probable that the difference between Cl and NO_2 lies not so much in their respective electron affinities as in the circumstance that Cl possesses free electrons, whereas the N of NO_2 does not. Therefore in C–Cl there may be occasional phases, non-existent in the case of $C–NO_2$, in which the co-valency with the carbon atom is increased, or alternatively, in which the electron density in the neighbourhood of the carbon atom is increased by the chlorine atom to such an extent that a co-valency change would occur if an electron-seat were available. The C–Cl group is thus the more plastic, and the electric intensity of the external fields varies over a greater range. This condition would be sufficient to account for such facts as the predominating *op*-

substitution of $Ph{\cdot}CH_2{\cdot}Cl$ as compared with the *mp*-substitution of $Ph{\cdot}CH_2{\cdot}NO_2$, even although the *average* electron affinities of Cl and NO_2 were approximately equal. The method of examination through a relay atom overcomes this difficulty to a large extent, because the phases at the C–Cl group that favour the reaction examined cannot be effective unless they happen to synchronise with a phase of the relay atom ($\overset{\curvearrowright}{\mathrm{O{-}C}}$ in the cases considered in this communication) also promoting reaction. It is obvious that this requirement must augment the relative importance of the normal conditions and diminish the magnitude of effects of the infrequent phases, $\overset{\curvearrowleft}{\mathrm{C{-}Cl}}$ and $\mathrm{C}\longleftarrow\mathrm{Cl}$.

EXPERIMENTAL.

Shoesmith and Slater (J., 1926, 219) obtained *m*-chlorobenzyl bromide, b. p. 109°/10 mm., from *m*-nitrobenzaldehyde through *m*-chlorobenzaldehyde and *m*-chlorobenzyl alcohol, which was treated with hydrogen bromide in benzene solution. We have employed two methods: (*A*) Aceto-*p*-toluidide ⟶ 3-chloro-*p*-toluidine (Chattaway and Orton, J., 1900, **77**, 792) ⟶ 2-chloro-4-methylphenylhydrazine ⟶ *m*-chlorotoluene ⟶ *m*-chlorobenzyl bromide (by refluxing with the theoretical amount of bromine). (*B*) *m*-Nitrobenzyl alcohol ⟶ *m*-aminobenzyl alcohol (Lutter, *Ber.*, 1897, **30**, 1065) ⟶ *m*-chlorobenzyl alcohol (in excellent yield) ⟶ *m*-chlorobenzyl bromide (by means of bromine and red phosphorus, compare Part II, *loc. cit.*). Both processes yielded an oil, b. p. 120—123°/24—25 mm., and the specimens were identified by conversion into 5-nitro-2-*m*-chlorobenzyloxyanisole, m. p. 121°. A mixture of the two specimens melted at the same temperature.

p-Chlorobenzyl bromide was obtained by the bromination of *p*-chlorotoluene (44 g.) (Jackson and Field, *Ber.*, 1878, **11**, 905). After crystallisation from 85% alcohol, 15 g. of nearly colourless needles, m. p. 50°, were obtained (Shoesmith and Slater, *loc. cit.*, give m. p. 51°). The following guaiacol and nitroguaiacol ethers were prepared by methods closely resembling those employed previously (Part II, *loc. cit.*) for the corresponding *m*- and *p*-nitrobenzyloxy-derivatives. The crude products never melted more than 1° lower than the true m. p., but were recrystallised two or three times, a process which did not alter the m. p.'s.

2-m-*Chlorobenzyloxyanisole*, $MeO{\cdot}C_6H_4{\cdot}O{\cdot}CH_2{\cdot}C_6H_4Cl$, b. p. 207—208°/15 mm., crystallised from light petroleum in slender needles, m. p. 46—47° (Found: C, 67·2; H, 5·4. $C_{14}H_{13}O_2Cl$ requires C, 67·6; H, 5·3%). It is readily soluble in most organic solvents.

4-*Nitro*-2-m-*chlorobenzyloxyanisole*, $MeO{\cdot}C_6H_3(NO_2){\cdot}O{\cdot}CH_2{\cdot}C_6H_4Cl$, crystallises from alcohol in minute, slender, colourless needles, m. p. 129—130·5° (Found: Cl, 12·3. $C_{14}H_{12}O_4NCl$ requires Cl, 12·1%).

5-*Nitro*-2-m-*chlorobenzyloxyanisole* crystallises from alcohol in colourless, feathery needles, m. p. 121° (Found : C, 57·0; H, 4·4. $C_{14}H_{12}O_4NCl$ requires C, 57·2; H, 4·1%).

2-p-*Chlorobenzyloxyanisole* crystallises from methyl alcohol in colourless, rectangular prisms, and from light petroleum in large, very well-defined prisms, m. p. 70° (Found : Cl, 14·3. $C_{14}H_{13}O_2Cl$ requires Cl, 14·3%). A description of these (Fig. 1) is contributed by Mr. H. E. Buckley, of the Crystallography Department of this University.

FIG. 1.

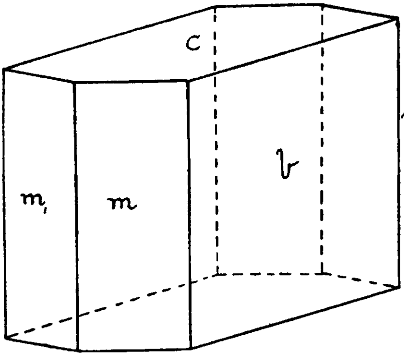
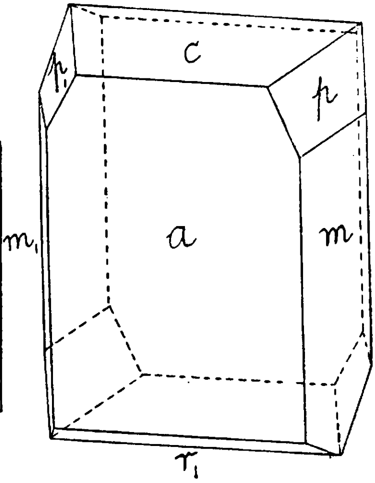


FIG. 2.



Symmetry : rhombic. Axial ratios : $a:b:c = 0{\cdot}7054:1:0{\cdot}7013$. Forms developed : *b*(010, tabular), *c*(001), *m*(110); (011) is very rare. Mean angular values : 011—001, 35° 3′ (6 angles; limits, 35° 0′—35° 12′); 010—110, 54° 48′ (24 angles ; limits, 54° 35′—55° 1′). Cleavage : imperfect, parallel to 100.

4-*Nitro*-2-p-*chlorobenzyloxyanisole* crystallises from alcohol in colourless, lustrous, feathery needles, m. p. 115—117° (Found : Cl, 11·8%).

5-*Nitro*-2-p-*chlorobenzyloxyanisole* crystallises from alcohol in colourless, flat needles, m. p. 120—120·5° (Found : Cl, 12·0%). Mr. Buckley has kindly examined the crystals (Fig. 2) deposited on slow evaporation of a solution in light petroleum.

System : monoclinic prismatic. Axial ratios : $a:b:c = 2{\cdot}699:1:1{\cdot}708$. $\beta = 74°\ 40'$. Habit : somewhat tabular on *a*(100). Forms generally developed : *a*(100), *m*(110), *r*($\bar{1}01$), *c*(001), and *p*(111). Mean angular values (calculated values in parentheses): *ac* 74° 40′, *am* 68° 59′, *ra* 69° 5′, *mc* 84° 37′ (84° 33′), *mr* 36° 15′ (36° 15′), *m* (110) *m*′ ($1\bar{1}0$) 42° 3′ (42° 3′), *pc* 56° 12′ (56° 1′).

Mixtures of 4- *and* 5-*Nitro*-2-m-*chlorobenzyloxyanisoles.*—The following freezing points were observed, the first number of each pair indicating the % of the 5-nitro-isomeride in the mixture: 15·36, 123·7° (1); 22·62, 119·85° (2); 30·42, 115·05° (3); 38·09, 110·0° (4); 43·12, 106·0° (5); 46·34, 103·65° (6).

Nitration of 2-m-*Chlorobenzyloxyanisole.*—The conditions given for the nitration of 2-*p*-nitrobenzyloxyanisole (Part II, *loc. cit.*, p. 389) were followed exactly. 1·7214 G. of the ether gave 2·0119 g. of the dried nitration product (yield, 99·0%), which was almost colourless and melted to a transparent liquid only slightly darker than that formed on fusion of the pure nitro-ethers. The filtrate and washings from the nitration were colourless and gave no coloration on the addition of sodium hydroxide. Since this product was found to behave as a binary mixture, it was not considered necessary to purify it by washing with methyl alcohol or in any other way. The f. p. of the nitration product was 107·55°, and from the graph we find: 5-nitro-isomeride, 41·1% [the Lagrange interpolation formula gave 41·3%, from points (2) to (5) inclusive]. A mixture of the nitration product (1·3779 g.) and the 4-nitro-isomeride (0·4796 g.) had f. p. 115·1°, practically coinciding with point (3) (30·42% of the 5-nitro-isomeride) and showing 40·9% of the 5-nitro-isomeride in the nitration product. A mixture of the nitration product (1·3779 g.) and the 4-nitro-isomeride (0·7884 g.) froze at 117·9° (5-nitro-isomeride, 25·95% from the graph), giving 40·8% of the 5-nitro-isomeride in the nitration product. A mixture of the 5-nitro-isomeride (0·6151 g., 41%) and of the 4-nitro-isomeride (0·8865 g.) froze at 107·8°, whilst the addition of 4-nitro-isomeride (0·5494 g.), reducing the 5-nitro-isomeride to 30·0%, raised the f. p. to 115·4°. These observations confirm those used in constructing the graph, and it appears that the nitration product contains 41% of the 5-nitro-isomeride. Hence the directive power of the *m*-chlorobenzyloxy-group is 69·5 (MeO = 100).

Mixtures of 4- *and* 5-*Nitro*-2-p-*chlorobenzyloxyanisoles.*—The following freezing points were observed, the first number of each pair indicating the % of the 5-nitro-isomeride in the mixture: 0, 116·3° (1); 9·8, 111·25° (2); 20·48, 106·0° (3); 32·26, 99·25° (4); 36·73, 95·6° (5); 44·86, 89·55° (6); 49·82, 84·8° (7). In (7) the first f. p. was 84·8°; the temperature then fell to 84·6°, and gradually rose to 86·05°, at which it remained constant for several minutes. This behaviour indicates the formation of an equimolecular compound of the components.

Nitration of 2-p-*Chlorobenzyloxyanisole.*—Except for the numerical details, the remarks made above on the *m*-isomeride are applicable to this case in every respect. (*a*) 1·9816 G. gave 2·3169 g. of the dried nitration product (yield, 99·0%) (Found: C, 57·1; H, 4·1. Calc. for $C_{14}H_{12}O_4NCl$: C, 57·2; H, 4·1%). (*b*) 1·2848 G. gave 1·4942 g. (yield, 98·5%). Nitration product (*a*) froze at 89·15°, (*b*) at 89·0°, and the f. p. 89·1° corresponds on the graph to 45·4% of the 5-nitro-isomeride. Mixtures of the nitration product (1·4424 g.) with the 4-nitro-isomeride (0·3487 g. and 0·6065 g.) had f. p.'s 96·0° and 99·55°, respectively. Both these values are very close to determined points (5 and 4 respectively): the first corresponds to 36·24% of the 5-nitro-isomeride, giving 45·0% of this in the nitration product, and the second to 31·74% of the 5-nitro-isomeride, giving 44·8% in the nitration product. The f. p. of a mixture of the 5-nitro-isomeride (0·7226 g., 44·85%) and the 4-nitro-isomeride (0·8884 g.) was 89·2°. Hence the nitration product contains 45% of the 5-nitro-isomeride, and the directive power of the *p*-chlorobenzyloxy-group is 82 (MeO = 100).

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