

Orientation in the Nitration of Benzaldehyde

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In connection with an investigation of isomer distributions in the nitrations of *-I-M* substituted thiophenes,^{1,2} the corresponding data with respect to benzaldehyde, benzonitrile, and nitrobenzene were of interest. The directing effects of the cyano and the nitro groups in aromatic nitration have recently been investigated.^{3,4} For benzaldehyde the fraction of the *meta* and the sum of the fractions of the *ortho* and *para* isomers obtained in nitration are reported by Baker and Moffitt.⁵ They were not able, however, to establish the *o:p* ratio, *i.e.* no complete information regarding the isomer distribution obtained in the nitration of benzaldehyde has hitherto been available. In the present work the isomer distributions obtained in the nitrations of these deactivated benzene derivatives are determined with gas chromatography. The reactions were carried out in trifluoroacetic acid solution, the medium used in the thiophene experiments.¹ Trifluoroacetic acid (TFA) has recently been used in the nitration of toluene by Brown and Wirkkala,⁶ who found no significant difference in the isomer composition as compared to that obtained in other media used in toluene nitrations.

The results are given in Table 1 together with isomer distributions obtained in nitration of benzonitrile³ and nitrobenzene⁴ in sulfuric acid. For comparison the isomeric compositions obtained in positive chlorination⁷ of the present benzene derivatives are included in Table 1.

Nitration of benzaldehyde in sulfuric acid at +5°C gives 85 % *meta* substitution.⁵ Using fuming nitric acid without any solvent, 72 % of the *meta* isomer is obtained at -9°C.⁵ Taking the temperature dependence into account, nitration of benzaldehyde in TFA (Table 1) would give 69 % of the *meta* isomer at about 0°C.

Thus changing TFA for sulfuric acid causes a significant increase of the fraction of *meta* nitration of benzaldehyde. The same solvent change for the benzonitrile and the nitrobenzene nitrations does on the contrary affect the fractions of *meta* substitution with only 2 % (when temperature effects are accounted for). Comparison of the fractions of *meta* nitrobenzonitrile obtained at 0° in sulfuric acid and in pure nitric acid shows a similar small difference.³

The accentuated sulfuric acid induced increase of the fraction of *meta* nitration of benzaldehyde as compared to the other two benzene derivatives may well be due to protonation of the aldehydic substituent group. The resulting increase of positive charge of the substituent would then be expected to strengthen its *meta* directing properties.

According to Table 1 the *m:o* ratio increases in the order of the substituents CHO < CN < NO₂ for the two reactions considered. This trend reflects the increas-

Table 1. Isomeric compositions.

	Temp. °C	Benzaldehyde			Benzonitrile			Nitrobenzene		
		% <i>o</i>	% <i>m</i>	% <i>p</i>	% <i>o</i>	% <i>m</i>	% <i>p</i>	% <i>o</i>	% <i>m</i>	% <i>p</i>
tration ^a	25	31 ± 2	67 ± 1	2.1 ± 0.4	17.8 ^b	78.4 ^b	3.7 ^b	6.1 ^c	92 ^c	2.06 ^c
tration ^a	75	32 ± 3	63 ± 3	4.3 ± 0.2	25 ± 4	70 ± 4	4.4 ± 1	10.5 ± 0.5	84.7 ± 0.5	4.8 ± 0.4
lorination ⁷	25	30.7	63.5	5.8	23.2	73.9	2.9	17.6	80.9	1.5

In TFA unless otherwise stated.

Values extrapolated to 25°C using data of Ref. 3 (sulfuric acid solution).

Values from Ref. 4 (sulfuric acid solution).

ing electron attraction of the substituents in the order given. Using a two atom substituent MO model it was possible to account for the trends in the *m:o* and the *m:p* ratios by simply increasing the Coulomb integral of the benzene carbon atom to which the substituent is attached. The correlations were based on the MO calculation (ω -technique) of the corresponding localization energies.³ Using the localization energies the partial rate factors are predicted to be of the order of 10^{-5} which is in reasonable agreement with the experimental values being of the order of 10^{-8} for nitrobenzene.⁴

From Table 1 is seen that the direction of change of the *m:o* ratio of nitrobenzene is such that the bulkiness of the nitro group is likely to be of consequence. The *m:o* ratios of benzaldehyde and of benzonitrile are much less sensitive towards changes of temperature and of the attacking electrophile (Table 1).

According to Table 1 the *o:p* ratio decreases for nitration in the order of the substituents $\text{CHO} > \text{CN} > \text{NO}_2$. For positive chlorination⁷ this order is reversed, however. There is no obvious reason why the two reactions should behave differently in this respect, in particular it is surprising that the *o:p* ratio of benzaldehyde is lower for chlorination as compared to nitration (Table 1). It should be remembered, however, that in the present cases the smallness of the fraction of *para* substitution (less than 5 %) makes the determination of the *o:p* ratio subject to considerable uncertainty. It has earlier been claimed⁷ that the trends of the *o:p* ratios are the same for nitration and for positive chlorination of the present benzene derivatives. But, as noted by the authors,⁷ the quoted values of the isomer distributions in the benzaldehyde and nitrobenzene nitrations were not obtained with modern analytical techniques. Moreover, the *o:p* ratio in the nitration of benzaldehyde could only be estimated from the data⁵ available at that time.

Experimental. The gas chromatographic analyses were made with an Aerograph model 1520 gas chromatograph equipped with a flame ionization detector and with a QF 1 column

(3% QF 1; $1/8" \times 2$ m; 160°C ; 20 ml N_2/min). Benzaldehyde, benzonitrile, and nitrobenzene were commercial products, redistilled before use, and their purity was checked with GLC. Before distillation the benzaldehyde sample was shaken with sodium bicarbonate solution.

For each nitration experiment 1 ml of ca. 1 M solution of the benzene derivative in TFA was kept in the constant temperature bath for about 5 min. Then 0.2 ml of ca. 12 M solution of fuming nitric acid (Merck, *p.a.*, $d=1.52$) in TFA was added. Thus the reaction mixtures at start were 1.13–1.54 M with respect to the benzene derivative and 2.44–2.49 M with respect to nitric acid. Aliquots were then withdrawn at suitable intervals and subsequently directly analyzed with GLC. The reactions were in none of the experiments allowed to go to completion; there was always a substantial amount of starting material left in the reaction mixture. Using authentic samples of the various nitroisomers the GLC peaks were identified mass spectrometrically (LKB 9000 gas chromatograph-mass spectrometer) in the benzaldehyde and the nitrobenzene cases and with the addition method in the benzonitrile case.

The detector sensitivity was found to be the same for the three isomers of the benzene derivative in question. The isomeric compositions found from evaluation of the peak areas are given in Table 1, where the errors in the figures are standard deviations of at least three aliquots.

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