738. *The Reactions of Organic Derivatives of Elements Capable of Valency-shell Expansion. Part X.* * *Partial Rate Factors for the Nitration of Benzyltrimethyl-phosphonium and -arsonium Picrates.*

By Frank L. Riley and Eugene Rothstein.

Benzyltrimethylphosphonium and benzyltrimethylarsonium picrates have been mononitrated in nitromethane solution, first alone in order to obtain isomer distributions, and then in competition with chlorobenzene. From this, the overall rates of nitration and the partial rate factors for each nuclear position have been calculated. Relative to benzene total deactivation is greater for the phosphonium than for the arsonium salt but on the other hand deactivations at the respective *meta*-positions are in the reverse order. The partial rate factors for the *para*-positions of both compounds are significantly larger than those of the corresponding *meta*-positions but the difference between the rates of *ortho* and *meta* is small. It is suggested that a reactivation process is present which is dependent on hyperconjugative effects associated with the valency-shell expansion of the phosphorus and arsenic atoms.

PRELIMINARY considerations leading to this work were discussed in Part IX and in this Paper attention is directed to the nitrations of trimethylphosphonium and trimethylarsonium picrates.[1] The nitration procedures described here and the quantitative estimation of the products were generally analogous to those already employed for ethyl phenyl and ethyl benzyl sulphones (Part IX) but modifications were necessitated by the presence of nitric and picric acids in the solutions of the nitrated products. Since benzyltrimethylphosphonium hydroxide undergoes a smooth decomposition into toluene when its aqueous solution is evaporated,[2] a corresponding reaction of the nitro-derivatives would have afforded mixtures of nitrotoluenes which could easily have been separated from other materials. This decomposition, however, was not quantitative and it gave variable yields of products; the method therefore was abandoned in favour of first removing the picric acid by extraction and then replacing the nitrate ion by means of a suitable ion exchange resin. Artificial mixtures afforded accurate and reproducible results but in actual nitrations by using acetyl nitrate in acetic anhydride it was found that the ion exchange resin irreversibly absorbed nitroacetic acid and other similar substances. It thus became desirable to replace the above reagents by solutions of pure nitric acid in nitromethane. This change reduced the rate of nitration and also altered somewhat the proportions of isomers, the reduction in the partial rate factors being approximately 10%.[3] However, this disadvantage was counter-balanced by the increased accuracy of the determinations and by the greater ease in obtaining the products. Owing to the disparity in their rates of nitration, direct competitive nitration between the phosphonium or arsonium picrates and benzene was precluded and consequently chlorobenzene was used as an intermediate. Fortunately the value for the ratio $K_{\text{PhCl}}/K_{\text{benzene}}$ in nitromethane was available.[3]

DISCUSSION

A summary of the results is recorded in Table 1 which also includes, for comparison purposes, the corresponding values for benzyl chloride, benzyl ethyl sulphone, benzyl cyanide, and nitrophenylmethane, the last four being figures for nitrations by acetyl nitrate in acetic anhydride.

All the above, except nitrophenylmethane, are phenyl derivatives with a $-I$, $+T$, type

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* Part IX, preceding Paper.

[1] Cf. Ingold, Shaw, and Wilson, *J.*, 1928, 1280.
[2] Fenton and Ingold, *J.*, 1929, 2342.
[3] Bird and Ingold, *J.*, 1938, 918.

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TABLE 1.

Orientation and partial rate factors for the nitration of benzyl derivatives, $PhCH_2X$, at 25°.

Group X	K_X/K_{PhH}	Isomers (%)			Partial rate factors		
		o	*m*	*p*	*o*	*m*	*p*
$^+PMe_3(pic^-)$ ...	0·0066	13·1	19·4	67·5	0·0026	0·0039	0·0268
$^+AsMe_3(pic)$ ...	0·0127	17·5(4)	6·7(4)	75·7(3)	0·0067	0·0026	0·0577
Cl [4] *..............	0·711	33·6	13·9	52·5	0·716	0·296	2·24
CN [4]..............	0·345	24·4	20·1	55·5	0·252	0·208	1·15
NO_2 [4]	0·122	22·5	54·7	22·8	0·0822	0·200	0·167
SO_2Et [5]	0·229	35·6	21·9	42·5	0·245	0·150	0·584

* For these comparisons the values of Knowles and Norman were considered to be more appropriate than those of Ingold and Shaw.

of substituent, classified by Ingold [6] as type 3, and characterised by (*a*) an overall deactivation relative to benzene and (*b*) a predominant *ortho-para* orientation. The latter is considered to be associated with a polarisability effect due to hyperconjugation of the methylene hydrogen atoms whilst the overall deactivation (*a*) arises from the permanent polarisation ($-I$ effect) caused by the substituting group as a whole.[7]

There are a number of distinguishing features about the results for the phosphonium and arsonium derivatives.

(i) The deactivation associated with the "integral" central positive charges on phosphorus and arsenic is notably greater than for any of the remaining groups in Table 1. The real measure of this is the very small partial rate factors of the *meta*-position, smaller even than the value (0·0093) found for ethyl phenyl sulphone where the strongly electronegative sulphonyl group is attached directly to the nucleus.

(ii) The high proportion of *para*-nitro-derivative suggests that a strongly conjugative mechanism is operating.[8] It is well known that in aromatic substitution both electromeric and mesomeric effects selectively favour the *para*-positions. The very low partial rate factors for the *ortho*-positions particularly of the phosphonium salt could be taken to indicate very little reactivation at these points but the possibility of steric interactions makes such an inference rather tentative.

(iii) Electromeric effects ($+E$) which lower the energy of the transition states must be the principal factor in the reactivation process because, comparing the phosphorus and arsenic compounds, the increase in K_X/K_{Ph} observed for the arsenic salt is not reflected by a corresponding increase in the rate factor for the *meta*-position.

(iv) Although the difference is too small to be really reliable, the evidence such as it is, is not in accordance with the supposition that the $-I$ effect of a positive field decreases with increase of atomic number.[9] In this case, the evidence points the other way.*

(v) Reactivation of the *para*-position does not appear to be associated in any way with inductive effects. The ratio K_X/K_{PhH} is smaller for nitrophenylmethane than it is for either benzyl ethyl sulphone or for benzyl cyanide, yet there is no evidence of strong reactivation. Predominant *meta*-nitration (88%) of benzyltrimethylammonium picrate,[10] suggests that even if hyperconjugative effects are present they must be neglibly small, but confirmatory rate data are not available. On the other hand hyperconjugation must be operative to some extent in benzyl chloride, and cyanide, as well as benzyl ethyl sulphone for which the overall deactivation and the partial rate factors for the *meta*-positions are similar to the corresponding values for nitrophenylmethane.

* Our values for the proportions of isomers differ slightly from those of Ingold, Shaw, and Wilson,[1] because their nitrations were in nitric acid at $-17°$.

[4] Knowles and Norman, *J.*, 1961, 2938.
[5] Part IX, preceding Paper.
[6] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," G. Bell, London, 1953, p. 247.
[7] Ingold and Shaw, *J.*, 1949, 575.
[8] Ref. 6, pp. 264 and 267.
[9] Ref. 6, p. 232.
[10] Goss, Hanhart, and Ingold, *J.*, 1927, 250.

The foregoing leads to the conclusion that a polarisability effect associated with the approach of the nitronium ion depends on the hyperconjugation of the benzyl hydrogen atom (I) which lowers the energy of the transition state. Additional resonance energy is contributed by structures such as (II) and (III), (X = phosphonium or arsonium) which are consequential to the enlargement of the valency shells of X.

It is not clear why this process should be more effective for trimethylarsonium than for trimethylphosphonium because it might have been anticipated that owing to their more diffuse nature the $4d$ orbitals of arsenic would be less efficient in forming $2p$–$4d$ π-bonds than would the $3d$ orbitals of phosphorus in similar bond-formation. Experimentally, Doering and Hoffmann found that the rate of deuterium exchange of tetramethylphosphonium iodide is nearly 10 times that of tetramethylarsonium iodide.[11] It

(I)   (II)   (III)
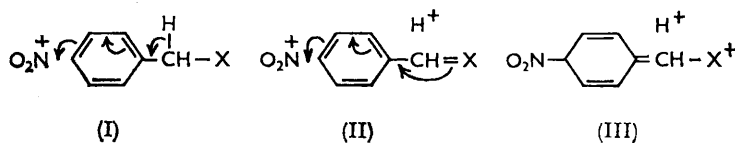
may be, however, that the approach of a nitronium ion brings into operation a polarisability effect which is greater for arsenic than for phosphorus thus leading to an increased drift of electrons towards the phenyl group.

EXPERIMENTAL

Preparation of Materials.—(*a*) Trimethylphosphonium salts were prepared from trimethylphosphine,[12] by condensing it with the appropriate benzyl derivatives followed by conversion of the product into the picrate.

(*b*) Benzyltrimethylarsonium picrate was prepared as described by Ingold, Shaw, and Wilson.[1] In order to prepare a mixture of nitration products for testing analytical procedures, the picrate (4 g.) was dissolved in nitric acid (*d* 1·53; 30 c.c.) at −78°. A dark red oil appeared which rapidly gave a pale yellow solution when shaken. The solution was warmed to −10° and kept there for 2 hr. after which, crushed ice (100 g.) was added, and the liquid neutralised (Congo Red) with gaseous ammonia. The precipitated mixed nitrobenzyltrimethylarsonium picrates were recrystallised (first, from aqueous acetone, then from acetone–ether), and then dried (P_2O_5) in a vacuum. The final m. p. was 170·5—171° (Found: C, 39·5; H, 3·4; N, 11·8. Calc. for $C_{16}H_{17}AsN_4O_9$: C, 39·7; H, 3·5; N, 11·6%).

(*c*) Individual nitrobenzyltrimethylarsonium picrates were prepared by boiling, under nitrogen, *o*-nitro- or *m*-nitro-benzyl iodide, or *p*-nitrobenzyl bromide, with ethereal trimethylarsine. The quaternary halides crystallised when the solutions were cooled and they were converted into the picrates as described above.

In both the phosphonium and arsonium series, the m. p.s of the picrates were appreciably higher than those recorded in the literature. Details are given below, with recorded m. p.s in parentheses.

Benzyltrimethylphosphonium picrate, m. p. 176—177° (173°) (Found: C, 48·8; H, 4·6; N, 10·4. Calc. for $C_{16}H_{18}N_3O_7P$: C, 48·6; H, 4·6; N, 10·6%).

Trimethyl-*o*-nitrobenzylphosphonium picrate, m. p. 153·5—154·5° (152—153°) (Found: C, 43·8; H, 3·9; N, 12·6. Calc. for $C_{16}H_{17}N_4O_5P$: C, 43·7; H, 3·9; N, 12·7%). *m*-Nitro-compound, m. p. 176—176·5° (171—172°) (Found: C, 43·8; H, 4·0; N, 13·0%). *p*-Nitro-compound, m. p. 194·5—195° (187—188°) (Found: C, 43·8; H, 3·9; N, 12·8%).

Benzyltrimethylarsonium picrate, m. p. 175·5—176° (175—176°) (Found: C, 43·7; H, 3·9; N, 9·0. Calc. for $C_{16}H_{18}AsN_3O_7$: C, 43·8; H, 4·1; N, 9·6%).

Trimethyl-o-nitrobenzylarsonium picrate, m. p. 149° (Found: C, 39·9; H, 3·6; N, 11·9. $C_{16}H_{17}AsN_4O_9$ requires C, 39·7; H, 3·5; N, 11·6%). *m-Nitro-compound*, m. p. 165·5° (Found: C, 39·7; H, 3·8; N, 12·0%). *p*-Nitro-*compound*, m. p. 172° (166—168°) (Found: C, 39·1; H, 3·8; N, 11·3%).

Analytical Procedures.—These in the main were similar to procedures described in the

[11] Doering and Hoffmann, *J. Amer. Chem. Soc.*, 1955, **77**, 521.
[12] Hibbert, *Ber.*, 1906, **39**, 160.

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previous Paper. The following modifications were necessary when estimating the phosphonium and arsonium compounds.

(a) *Removal of nitrate ions.* Nitrate ions were removed from nitration mixtures by passage of the solutions through columns of " Dowex-2 " basic anion exchange resins having a theoretical capacity of 3 mol.-equiv./g. when dry or 1·1 mol.-equiv./g. when wet. The mesh size used for phosphonium salts was 40—60, and for arsonium derivatives it was 100—200. The maximum rate at which solutions flowed through was 2—3 c.c./min., but for washing purposes, a slight vacuum (400—500 mm.) was applied to the lower end of the columns and the rate was increased to 7—10 c.c./min. The resins were prepared by washing them successively with 10% hydrochloric acid, water, and 10% carbonate-free sodium hydroxide and finally with water. The process was then repeated. Two types of column were used. The " acetate " column was prepared from the hydroxy-form by washing it with 10% acetic acid until it was completely neutralised. After use, it was regenerated into the hydroxy-form by washing it with sodium hydroxide until it was free from nitrate ion. The " chloride " column was similarly prepared using 10% hydrochloric acid. After use it was regenerated by washing it with the acid (2—3 l.) until the wash-liquors showed no u.v. absortion when balanced against distilled water. The presence of nitrates was detected in the conventional manner using a solution (0·5% w/w) of diphenylamine in 90% sulphuric acid. A faint blue colour was obtained after 1 min. when 2 drops of 0·0001-molar solution of nitrate ion was added to 0·5 c.c. of the reagent. The presence of acetic acid did not interfere with the test, nor were positive reactions given either by nitrobenzene in moderately large amounts or by the nitrobenzyl derivatives. The columns were regenerated after each experiment, but as a further precaution they were washed with distilled water just before use because there was a tendency for water to develop a moderately strong absorption below 250 mμ when it was left in contact with the exchange resin for any length of time.

(b) *Preparation of standard solutions of phosphonium and arsonium chlorides for u.v. analysis.* In testing the method of analysis, the pure picrates were converted into the chlorides by shaking the weighed samples with a mixture of 5% aqueous hydrochloric acid and 50% ethyl acetate–toluene. The aqueous layer was again extracted with small quantities of toluene until quite colourless, and the extracts washed by successive small quantities of 2% hydrochloric acid the combined aqueous layers being washed with toluene and added to the original aqueous layer. Picric acid was entirely removed, and titanous chloride titration showed a quantitative recovery of the phosphonium and arsonium salts. The aqueous extracts (200—250 c.c.) were reduced to approximately 100 c.c. by distillation, (40°/30 mm.) and then accurately made up to 250 c.c. with distilled water. The final solutions contained 0·00005—0·00006 mole/l. of the nitro-compounds. The concentration of the hydrochloric acid was adjusted to 0·05 mole/l.

(c) *Applicability of Beer's law.* The absorptions of different concentrations of the nitro-compounds were measured at a variety of wavelengths and were found to give a linear relationship between concentration and optical density.

Nitration of Benzyltrimethylphosphonium Picrate in Competition with Benzene.—(a) *Preliminary investigation into the paraffinic decomposition of trimethylnitrobenzylphosphonium hydroxide.* It was ascertained that there was complete recovery of pure *p*-nitrotoluene when it was distilled in steam from its mixture with dilute aqueous alkali, but steam distillation of alkaline solutions of the pure nitrobenzyltrimethylphosphonium picrates afforded variable yields (29—82%) of the corresponding nitrotoluenes and a method of estimation based on this reaction was clearly unreliable.

(b) *Estimation of artificial mixtures of nitrobenzene with trimethylnitrobenzylphosphonium picrates.* Initially, artificial mixtures containing all the products to be expected in a competitive nitration of the phosphonium picrate with benzene were examined. The mixtures were acidified by 10% HCl and shaken with benzene–ethyl acetate (3 : 1 solution) followed by pure benzene (6 × 15 c.c.). The combined organic layers were extracted with 2% HCl (3 × 10 c.c.), and after the combined aqueous layers had been freed from picric acid, as before, they were added to the original aqueous solution. Finally, the new benzene extracts were extracted with 2% HCl, and the aqueous layer washed with toluene (4 × 10 c.c.) and added to the previous ones. The toluene was discarded.

The solution of the nitro-phosphonium salts (150—200 c.c.) was passed through a column (50 c. × 2·4 cm. diam.) containing " Dowex-2 " acetate resin (40—60 mesh). It was at this stage it was found that in order to preserve the activity of the exchange resin it would

be desirable to replace acetic anhydride by nitromethane. Any phosphonium ion remaining on the column was eluted with water, tests for nitrate ion in the eluent being made at frequent intervals. The solution was then concentrated to 100 c.c. and run through a second column (10 cm. × 1·8 cm. diam.) to remove traces of nitrate ion which still remained. The liquid (400—500 c.c.) was now acidified by concentrated hydrochloric acid (2—3 c.c.) and its volume reduced by distillation (b. p. 30—40°/40—50 mm.) and the final solution (10—15 c.c.) diluted with methanol to 50 c.c. A check on the method was made by treating in the manner described above, two separate solutions each containing 0·01 mole sodium nitrate, and 0·001570 and 0·0001809 mole respectively of the nitrobenzylphosphonium chlorides. These gave aqueous solutions of the phosphonium salts (recovery 99·4 and 99·8%) containing less than 0·0000025 mole of nitrate ion. The foregoing method was adopted for solutions both in acetic anhydride and in nitromethane. In recovering the nitrobenzene, there was a small difference in procedure. In this case, after the organic extracts had been washed successively with 10% aqueous sodium carbonate (2 × 50 c.c.), 10% potassium hydroxide (2 × 50 c.c.) and water, (3 × 50 c.c.), further washes with sodium sulphite and sodium hydrogen carbonate solutions were included for the cases where acetic anhydride was the solvent. Otherwise the last two were omitted. The usual precautions were taken that no nitrobenzene was left in the aqueous layers, and finally the organic layers were dried (CaCl$_2$) and concentrated by slow distillation through a Dufton column. The residual liquid (15—20 c.c.) was diluted to 100 c.c. with methanol. The results for artificial mixtures in acetic anhydride were reasonably good, but in nitromethane erratic results for nitrobenzene were traced to the nitromethane which had been purchased in the ordinary way and contained at least 0·1% of non-acidic nitro-impurities. These were not positively identified, but nitrous acid was detected when hot concentrated sulphuric acid was added to the material, which also showed an absorption peak in the infrared spectrum, at 5·87 μ. Tentatively it is suggested that the specimen contained 2-nitropropane, 2-methyl-2-nitropropane, and *ca.* 0·1% diethyl ketone. Nitromethane prepared from chloro-acetic acid was completely free from these substances and when used as a solvent proved satisfactory, the mean deviation for nitrobenzene being 0·43%. The nitro-compounds were estimated by titanous chloride titration (Part IX).

(c) *Nitration of benzyltrimethylphosphonium picrate in competition with* (i) *benzene and* (ii) *chlorobenzene.* Nitric acid (*d* 1·529; 0·05 mole) was slowly added with shaking to a mixture of benzyltrimethylphosphonium picrate (0·005 mole), benzene (0·005 mole), and nitromethane (0·09 mole) at −70°. The homogeneous solution which was formed after addition of the acid was stirred and the temperature raised to 25 ± 0·02°. Stirring was continued until the end of the reaction, the liquid was then added to ice–water and the products analysed. The results, Table 2 (i), showed that owing to its high rate of nitration, benzene had virtually disappeared towards the end of the reaction after which non-competitive nitration of the phosphonium salt had occurred. Benzene was therefore replaced by chlorobenzene and the nitration repeated, the method of isolation and analysis being unchanged. Not unexpectedly, the calculated rate of nitration, Table 2 (ii), relative to benzene, was smaller than the figure previously obtained but of the same order.

TABLE 2.

Nitration of benzyltrimethylphosphonium picrate in competition with (i) benzene, (ii) chlorobenzene, by nitric acid in nitromethane.

Initial Quantities: HNO$_3$ (*d* 1·529), 0·05 mole; MeNO$_2$, 0·09 mole. PhCH$_2$·$\overset{+}{P}$Me$_3$ Pic. = PhH = PhCl = 0·005 mole. Temp., 25 ± 0·02°. Quantities of NBTP (nitro-phosphonium salt), PhNO$_2$, and chloronitrobenzene (CNB) expressed in 10^5 mole.

		(i) With benzene.					(ii) With chlorobenzene.		
No.	Time (hr.)	NBTP	PhNO$_2$	K/K_{PhH}	No.	Time (hr.)	NBTP	CNB	K/K_{PhCl}
1	37	77·4	495·8	0·035	4	17	64·7	241·4	0·210
2	20	24·8	486·8	0·014	5	14	60·1	222·7	0·218
3	18	40·6	486·1	0·024	6	16	58·7	219·5	0·216
					7 *	14	55·8	232·6	0·215
					8 *	16	55·8	239·1	0·207
					9 †	26	62·3	240·0	0·204

* 0·00550 mole of chlorobenzene used.   † 0·10 mole of nitromethane used.

Mean value for K_{BTP}/K_{PhCl} = 0·212 ± 0·0018. Since in nitromethane K_{PhCl}/K_{PhH} = 0·0312 ± 0·0006^3. Hence K_{BTP}/K_{PhH} = 0·00661 ± 0·00013.

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TABLE 3.

Optical densities and ratios of pure trimethylnitrobenzylphosphonium chlorides dissolved in 0·05N-hydrochloric acid. Concentrations (10^5 mole/l.): *ortho*, 5·97; *meta*, 6·74; *para*, 5·52.

The symbols A_m/A_o, R/A_o', etc., have the same significance as in Part IX.

λ (mμ)	D (o)	D (m)	A_m/A_o	D (p)	A_p/A_o	λ (mμ)	D (o)	D (m)	A_m/A_o	D (p)	A_p/A_o
210	0·771	—	—	—	—	255	0·295	0·450	1·525	0·433	1·468
215	0·514	—	—	—	—	260	0·326	0·503	1·543	0·516	1·583
220	0·395	0·507	1·283	0·304	1·034	265	0·341	0·521	1·528	0·578	1·695
225	0·310	0·287	0·926	0·178	0·574	270	0·332	0·498	1·500	0·604	1·819
227	0·270	0·214	0·791	0·154	0·570	275	0·306	0·442	1·448	0·593	1·938
230	0·214	0·185	0·864	0·142	0·663	280	0·269	0·366	1·361	0·545	2·026
233	0·179	0·178	0·994	0·152	0·849	285	0·230	0·290	1·261	0·474	2·061
235	0·170	0·188	1·096	0·160	0·936	287	0·215	0·264	1·225	0·443	2·060
237	0·169	—	—	—	—	290	0·196	0·224	1·143	0·394	2·010
240	0·180	0·238	1·322	0·212	1·128	295	0·168	0·176	1·048	0·314	1·869
245	0·210	0·304	1·452	0·266	1·273	300	0·146	0·139	0·952	0·243	1·664
250	0·251	0·379	1·510	0·344	1·371	310	0·109	0·085	0·780	0·123	1·128

TABLE 4.

Optical densities of mixed trimethylnitrobenzylphosphonium chlorides from the nitration of benzyltrimethylphosphonium picrate in nitromethane by nitric acid at 25°.

λ (mμ)	Nitration 1			Nitration 2			Nitration 3		
	D	R/A_o	R/A_o'	D	R/A_o	R/A_o	D	R/A_o	R/A_o'
225	—	—	—	—	—	—	0·212	0·684	0·276
227	0·169	0·628	0·252	—	—	—	—	—	—
230	0·150	0·701	0·263	—	—	—	0·158	0·738	0·268
233	0·150	0·839	0·280	—	—	—	0·160	0·894	0·292
235	0·155	0·911	0·295	—	—	—	0·169	0·988	0·325
245	0·248	1·181	0·342	—	—	—	—	—	—
255	0·315	1·257	0·354	0·463	1·569	0·439	0·211	1·122	0·407
260	0·459	1·407	0·361	0·542	1·663	0·444	—	—	—
265	0·511	1·482	0·362	0·596	1·748	0·443	0·543	1·592	0·389
270	0·517	1·557	0·356	0·606	1·825	0·425	0·557	1·678	0·390
275	0·495	1·618	0·340	—	—	—	0·535	1·748	0·374
280	0·448	1·666	0·328	0·528	1·963	0·423	0·484	1·799	0·359
285	0·386	1·678	0·316	0·454	1·974	0·387	0·416	1·809	0·343
287	0·360	1·674	0·312	0·424	1·972	0·386	0·388	1·805	0·342
290	0·319	1·628	0·302	0·376	1·918	0·370	0·344	1·755	0·329
295	—	—	—	0·310	1·792	0·354	—	—	—
300	0·200	1·370	0·288	0·235	1·609	0·328	0·214	1·466	0·383
310	0·107	0·986	0·241	0·126	1·166	0·298	0·115	1·055	0·253

λ (mμ)	Nitration 4			Nitration 5		
	D	R/A_o	R/A_o'	D	R/A_o	R/A_o'
225	0·217	0·700	0·290	0·197	0·635	0·245
227	0·186	0·689	0·279	0·167	0·618	0·231
230	0·160	0·748	0·275	0·146	0·682	0·231
233	0·159	0·888	0·294	0·149	0·832	0·257
235	—	—	—	0·157	0·918	0·273
245	0·267	1·277	0·361	0·250	1·196	0·334
250	0·343	1·366	0·375	—	—	—
255	0·420	1·424	0·373	0·397	1·346	0·346
260	0·448	1·497	0·375	0·465	1·426	0·348
265	—	—	—	0·510	1·496	0·348
270	0·539	1·623	0·362	0·523	1·575	0·337
275	0·520	1·699	0·353	—	—	—
280	0·470	1·747	0·354	—	—	—
285	0·404	1·756	0·333	0·391	1·700	0·387
287	0·376	1·749	0·330	0·365	1·698	0·298
290	0·355	1·709	0·313	0·323	1·648	0·282
295	0·269	1·601	0·310	0·259	1·542	0·272
300	—	—	—	0·202	3·383	0·252
310	0·115	1·055	0·243	0·108	0·991	0·222

Nitration of Benzyltrimethylphosphonium Picrate Alone.—The nitrations were carried out in nitromethane employing the conditions described for competitive reactions but omitting chlorobenzene. The nitro-phosphonium salts were isolated as the chlorides using the chloride ion-exchange column, and the final solutions diluted so as to give 0·05N-hydrochloric acid solutions containing 0·00005—0·00006 mole/l. of the phosphonium salt. The isomer distributions were obtained from the u.v. absorption spectra (Table 4) of the nitration products, used in conjunction with the absorption spectra of the pure nitro-derivatives (Table 3), as described in Part IX. Artificial mixtures of the three nitro-compounds using the same method showed mean deviations of *ortho*, 0·5%; *meta*, 0·97% *para*, 0·47%.

The proportions of isomers was calculated as indicated in Part IX from the equation $R/A_o = x_o/c_o + x_m/c_m . A_m/A_o + x_p/c_p . A_p/A_o$, c_o, c_m, and c_p being the concentrations of the *ortho-*, *meta-*, and *para*-isomers of Table 3 and x_p/c_p having a value necessary for a plot of R/A_o against A_m/A_o to be a straight line of which the intercept is x_o/c_o and the slope x_m/c_m. The results are depicted in Table 5.

TABLE 5.

Percentages of isomers formed in the nitration of benzyltrimethylphosphonium picrate.
All concentrations expressed in 10^5 mole/l.

No.	x_o/c_o	o	x_m/c_m	m	x_p/c_p	p	Total isomers	Isomers (%)		
								o	m	p
1	0·138	0·824	0·143	0·964	0·660	3·643	5·431	15·2	17·7	67·1
2	0·153	0·913	0·189	1·274	0·770	4·250	6·437	14·2	19·8	66·0
3	0·104	0·621	0·189	1·274	0·710	3·919	5·814	10·7	21·9	67·4
4	0·148	0·884	0·148	0·997	0·720	3·974	5·855	15·1	17·0	67·9
5	0·092	0·549	0·168	1·132	0·680	5·754	5·435	10·1	20·8	69·1

Mean percentages: *ortho*, 13·1 ± 0·9; *meta*, 19·4 ± 0·7; *para*, 67·5 ± 0·3. The partial rate factors were therefore F_{ortho} 0·0026 ± 0·0002; F_{meta} 0·0039 ± 0·0001; F_{para} 0·0268 ± 0·0001.

Nitration of Benzyltrimethylarsonium Picrate in Competition with Chlorobenzene.—Experimental conditions were identical with those used for the nitration of the corresponding phosphonium salts. Artificial mixtures afforded mean deviations from the calculated results of 0·57 and 1·17% in the estimated quantities of arsonium picrates and chloronitrobenzenes, respectively.

In actual nitrations, the moisture content of the arsonium picrate had a significant effect on the figures obtained (nitrations 1—3). When the picrates were further dried (P_2O_5), a somewhat different set of self-consistent values were obtained (nitrations 4—6). Finally a completely fresh sample was dried at low pressures (P_2O_5) and two more determinations were carried out. All five (nos. 4—8) were therefore used in calculating the mean values of the isomer distribution, (Table 6).

Nitration of Benzyltrimethylarsonium Picrate alone.—There was no difference in the conditions of nitrations from those of the phosphonium salts. In the measurements of the u.v. absorptions of the experimental mixtures of nitro-compounds, however, the reference cell contained a

TABLE 6.

Nitration of benzyltrimethylarsonium picrate in competition with chlorobenzene by nitric acid in nitromethane.

Initial Quantities: HNO$_3$ (d 1·529), 0·05 mole; MeNO$_2$, 0·09 mole. PhCH$_2$·AsMe$_3$ Pic, = PhCl = 0·0050 mole. Temp. 25 ± 0·02°. Quantities expressed in 10^5 mole.

No.	Time (hr.)	TNBA	CNB	K/K_{PhCl}	No.	Time (hr.)	TNAB	CNB	K/K_{PhCl}
							P$_2$O$_5$ dried picrate		
1 *	12	92·3	214·7	0·364	4	17	111·2	228·7	0·412
2	12	76·3	182·8	0·363	5	16	116·0	238·4	0·407
3	24	107·3	239·3	0·371	6 †	22	114·0	262·3	0·401
					7	24	116·3	237·3	0·411
					8	27	125·3	252·8	0·410

Mean value K_{BTA}/K_{PhCl} (nos. 4—8) = 4·08 ± 0·014 and hence $K_{BTA}/K_{Benzene}$ = 0·0127 ± 0·0002.
    * 0·081 mole nitromethane used.   † 0·0050 mole chlorobenzene used.

Note: Chloronitrobenzene = CNB. Benzyltrimethylarsonium picrate = BTA. Trimethylnitrobenzylarsonium picrate = TNBA.

TABLE 7.

Optical densities and ratios of pure trimethylnitrobenzylarsonium chlorides dissolved in 0·05N-hydrochloric acid.

Concentrations (10^5 mole/l.): *ortho*, 7·90; *meta*, 5·49; *para*, 5·96.

λ (mμ)	D (o)	D (m)	A_m/A_o	D (p)	A_p/A_o	λ (mμ)	D (o)	D (m)	A_m/A_o	D (p)	A_p/A_o
220	0·674	0·695	1·031	0·350	0·519	270	0·427	0·407	0·953	0·648	1·518
225	0·485	0·382	0·788	0·209	0·431	275	0·402	0·364	0·905	0·669	1·664
226	0·452	0·336	0·743	0·187	0·414	280	0·359	0·306	0·852	0·649	1·808
228	0·390	0·265	0·679	0·158	0·405	283	0·333	0·268	0·850	0·620	1·862
230	0·332	0·212	0·638	0·141	0·425	285	0·313	0·243	0·776	0·596	1·904
232	0·281	0·177	0·630	0·137	0·188	287	0·296	0·219	0·740	0·570	1·926
234	0·242	0·158	0·653	0·140	0·578	290	0·270	0·189	0·698	0·521	1·930
235	0·228	0·154	0·675	0·144	0·632	293	0·250	0·162	0·648	0·473	1·892
236	0·219	0·155	0·708	0·150	0·685	295	0·238	0·148	0·622	0·437	1·836
240	0·209	0·178	0·852	0·182	0·871	300	0·213	0·118	0·554	0·352	1·653
245	0·237	0·227	0·958	0·238	1·004	305	0·192	0·096	0·500	0·266	1·385
250	0·289	0·289	1·000	0·317	1·100	310	0·173	0·077	0·445	0·193	1·116
255	0·346	0·350	1·012	0·407	1·176	315	0·151	0·061	0·404	0·132	0·874
260	0·395	0·398	1·008	0·506	1·281	320	0·130	0·048	0·369	0·089	0·685
265	0·423	0·417	0·986	0·591	1·397						

TABLE 8.

Optical densities of mixed trimethylnitrobenzylarsonium chlorides from the nitration of benzyltrimethylarsonium picrate in nitromethane by nitric acid at 25°.

Reference cell: (*p*-isomer) $5·96 \times 10^{-5}$ mole/l. in nitrations 1, 3, 4, and 5; $9·54 \times 10^{-5}$ mole/l. in nitration 2.

Nitration 1

λ (mμ)	D	R/A_o	R/A_o'	λ (mμ)	D	R/A_o	R/A_o'	λ (mμ)	D	R/A_o	R/A_o'
220	0·464	0·688	0·439	240	0·174	0·832	0·414	285	0·413	1·319	0·405
225	0·293	0·604	0·397	245	0·217	0·916	0·436	287	0·391	1·321	0·397
226	0·267	0·592	0·391	250	0·279	0·965	0·437	300	0·246	1·155	0·362
228	0·225	0·577	0·383	260	0·417	1·056	0·441	305	0·196	1·021	0·356
230	0·1935	0·583	0·382	265	0·466	1·102	0·431	310	0·151	0·873	0·337
232	0·171	0·608	0·374	270	0·494	1·157	0·428	315	0·114	0·755	0·336
234	0·1585	0·655	0·378	280	0·461	1·284	0·416	320	0·086	0·661	0·332
236	0·157	0·717	0·388	283	0·433	1·300	0·406	—	—	—	—

Nitration 2

λ (mμ)	D	R/A_o	R/A_o'	λ (mμ)	D	R/A_o	R/A_o'	λ (mμ)	D	R/A_o	R/A_o'
220	0·508	0·754	0·546	240	0·180	0·861	0·513	293	0·308	1·232	0·475
225	0·327	0·674	0·502	270	0·487	1·140	0·533	295	0·287	1·206	0·472
228	0·251	0·644	0·482	280	0·433	1·234	0·511	300	0·238	1·117	0·456
230	0·214	0·645	0·475	283	0·416	1·249	0·505	305	0·193	1·005	0·451
232	0·187	0·665	0·470	285	0·393	1·256	0·494	310	0·153	0·884	0·438
234	0·172	0·711	0·480	287	0·373	1·260	0·490	315	0·119	0·788	0·428
236	0·166	0·758	0·484	290	0·338	1·252	0·480	320	0·090	0·692	0·418

Nitration 3

λ (mμ)	D	R/A_o	R/A_o'	λ (mμ)	D	R/A_o	R/A_o'	λ (mμ)	D	R/A_o	R/A_o'
220	0·464	0·688	0·408	240	0·179	0·856	0·386	293	0·344	1·376	0·354
225	0·296	0·610	0·377	245	0·225	0·040	0·405	295	0·320	1·344	0·351
226	0·268	0·592	0·369	250	0·290	1·003	0·409	300	0·2615	1·228	0·335
228	0·226	0·579	0·360	260	0·435	1·101	0·409	305	0·208	1·083	0·335
230	0·1945	0·586	0·357	265	0·490	1·158	0·404	310	0·161	0·931	0·328
232	0·173	0·616	0·353	270	0·520	1·218	0·398	315	0·120	0·794	0·322
234	0·161	0·665	0·353	280	0·487	1·356	0·380	320	0·089	0·685	0·315
236	0·160	0·732	0·361	283	0·458	1·375	0·370	—	—	—	—

Nitration 4

λ (mμ)	D	R/A_o	R/A_o'	λ (mμ)	D	R/A_o	R/A_o'	λ (mμ)	D	R/A_o	R/A_o'
220	0·4395	0·652	0·387	245	0·211	0·890	0·378	290	0·359	1·330	0·346
225	0·280	0·577	0·357	255	0·343	0·991	0·391	293	0·327	1·308	0·343
226	0·254	0·562	0·351	260	0·411	1·040	0·387	300	0·249	1·169	0·326
228	0·215	0·551	0·344	265	0·463	1·095	0·383	305	0·198	1·031	0·325
230	0·184	0·554	0·337	270	0·4925	1·153	0·379	310	0·153	0·884	0·315
232	0·1635	0·582	0·333	280	0·462	1·287	0·365	315	0·114	0·755	0·309
234	0·153	0·632	0·337	285	0·416	1·329	0·358	320	0·085	0·654	0·305
240	0·1685	0·806	0·362	287	0·393	1·328	0·346	—	—	—	—

TABLE 8.   (*Continued.*)

Nitration 5

220	0·330	0·490	0·345	240	0·121	0·579	0·335	290	0·229	0·848	0·307
225	0·215	0·443	0·322	245	0·1505	0·635	0·354	293	0·208	0·832	0·302
226	0·195	0·431	0·315	250	0·193	0·668	0·360	295	0·195	0·819	0·305
228	0·164	0·420	0·307	260	0·282	0·714	0·355	300	0·161	0·756	0·293
230	0·140	0·422	0·303	270	0·328	0·768	0·343	305	0·130	0·677	0·289
232	0·124	0·441	0·304	280	0·300	0·836	0·330	310	0·102	0·590	0·278
234	0·113	0·467	0·305	285	0·266	0·850	0·317	315	0·0785	0·520	0·275
236	0·114	0·507	0·315	287	0·2530	0·855	0·316	320	0·060	0·461	0·269

TABLE 9.

Percentages of isomers formed in the nitrations of benzyltrimethylarsonium picrate.

All concentrations expressed in 10^5 mole/l.

No.	x_o/c_o	o	x_m/c_m	m	x_p/c_p	p	Total isomers *	Isomers (%)		
								o	m	p
1	0·269	2·125	0·168	0·922	0·480	2·861	11·868	17·90	7·77	74·33
2	0·358	2·828	0·183	1·005	0·400	2·384	15·757	17·95	6·38	75·67
3	0·263	2·078	0·143	0·785	0·540	3·218	12·041	17·26	6·52	78·22
4	0·256	2·022	0·129	0·708	0·510	3·040	11·730	17·24	6·04	76·72
5	0·221	1·746	0·128	0·703	0·280	1·669	10·078	17·32	6·98	75·70

* Including p isomer used in reference cell.

Mean percentages: *ortho*, 17·54 ± 0·31; *meta*, 6·74 ± 0·22; *para*, 75·73 ± 0·25.
The partial rate factors were therefore: F_{ortho}, 0·0067 ± 0·0001; F_{meta}, 0·0026 ± 0·0001; F_{para}, 0·0577 ± 0·0009.

solution of trimethyl-*p*-nitrobenzylarsonium chloride in 0·5N-hydrochloric acid (second column), in order to balance out the excessive proportion of this isomer. This procedure afforded reliable results, the mean deviations from the calculated amounts being *ortho*, 0·45%; *meta*, 0·20%; *para*, 0·65%.

The absorption spectra used for these determinations is given in Table 7, and the corresponding spectra for the nitration products in Table 8. Table 9 shows the proportions of isomers calculated from Tables 7 and 8.

THE UNIVERSITY, LEEDS.   [*Received, September 11th*, 1963.]