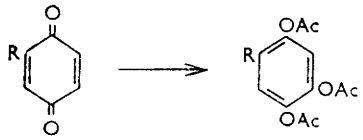
Thiele Acetylation of Quinones. Part II.[1] *p*-Benzoquinones with Halogen Substituents

By **J. M. Blatchly**, Charterhouse, Godalming, Surrey
J. F. W. McOmie* and **J. B. Searle**, School of Chemistry, The University, Bristol BS8 1TS

Thiele acetylation of all mono-, di-, and tri-bromo-*p*-benzoquinones, and of iodo- and 2,6-di-iodo-*p*-benzoquinone is described. Contrary to a previous report, 2,6-dichloro-*p*-benzoquinone readily undergoes Thiele acetylation. The assignments of orientation of some previously reported dibromotrimethoxy-benzenes have been shown to be erroneous.

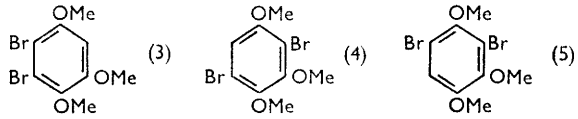
THE acid-catalysed reaction of quinones with acetic anhydride to give triacetoxy-compounds (Thiele acetylation), *e.g.* (1) → (2) (R = Me) has been known for many years.[2] This reaction applied to quinone † itself and to toluquinone, has been investigated by kinetic measurements, and proposals concerning the mechanism have been made.[3] Schweizer[4] has made calculations which relate the structure of polycyclic quinones to their reactivities in many reactions including Thiele acetylation. However, as far as we are aware, no general mechanism has been put forward which enables one to predict whether or not a substituted quinone will undergo the reaction, and what will be the orientation of the product or products if formed. The object of the investigations recorded in Parts I and II and in subsequent papers is to study the scope of the reaction with mono- and poly-cyclic quinones and thus to provide information on which a general theory can be based. Possible mechanisms and the effect of substituents will be discussed in a later paper.



(1) (2)

Only two halogeno-quinones have previously been studied in the reaction: 2-chloroquinone,[5] which was shown to give 1,2,4-triacetoxy-5-chlorobenzene (2; R = Cl),[6] and 2,6-dichloroquinone, which was stated by Fieser and Ardao [7,8] to be unreactive in acetic anhydride containing sulphuric acid as catalyst. We have found that the dichloroquinone gives a 60% yield of 1,2,4-triacetoxy-3,5-dichlorobenzene with boron trifluoride as catalyst, and that a faster reaction to give the same product occurs with sulphuric acid or with perchloric acid as catalyst. Thiele acetylation of 2-bromo- and 2-iodo-quinone gave 5-bromo- and 5-iodo-1,2,4-triacetoxybenzene respectively, as shown by combined hydrolysis and methylation of the acetates, which gave the known compounds 5-bromo- and 5-iodo-1,2,4-trimethoxybenzene.

The three isomeric dibromo-quinones reacted to give three isomeric dibromo-1,2,4-triacetoxybenzenes which were then converted into the corresponding dibromotrimethoxybenzenes. The orientations of the two known isomers of the dibromo-1,2,4-trimethoxybenzenes was uncertain when they were reported but we have now established the orientation of the three possible isomers with certainty. We have repeated the earlier work and have found that isomer (3), obtained *via* Thiele acetylation of 2,3-dibromoquinone, is identical with the product, m.p. 97°, obtained by Dorn, Warren, and Bullock[9] by bromination of 6-bromo-1,2,4-trimethoxybenzene and claimed by them to have structure (4). Isomer (5), obtained by us from 2,6-dibromoquinone is



identical with the product obtained but not orientated by Fabinyi and Széki,[10] by bromination of 5-bromo-1,2,4-trimethoxybenzene. Since bromination of 1,2,4-trimethoxybenzene is almost instantaneous at room temperature and gives the 5-bromo-derivative, whereas further bromination of this product is much slower and the bromine enters at position 3, the bromination of 6-bromo-1,2,4-trimethoxybenzene might be expected to occur preferentially (as in fact it does) at the 5- rather than the 3-position. As a further check on the orientations, some other reactions of the three isomers (3), (4), and (5), have been studied and are described in Part III.[11]

Thiele acetylation of 2,3,5-tribromoquinone proceeded much more slowly than that of the mono- or di-halogeno-quinones; in presence of boron trifluoride it gave the

† Throughout this paper the name quinone refers to *p*-benzoquinone unless otherwise indicated.

[1] The paper by J. M. Blatchly and J. F. W. McOmie, *J. Chem. Soc.*, 1963, 5311 is regarded as Part I of this series.

[2] J. Thiele, *Ber.*, 1898, **31**, 1247; J. Thiele and E. Winter, *Annalen*, 1900, **311**, 341.

[3] H. A. E. Mackenzie and E. R. S. Winter, *Trans. Faraday Soc.*, 1948, **44**, 159, 171, 243.

[4] H. Hopff and H. R. Schweizer, *Helv. Chim. Acta*, 1962, **45**, 312, 1044; H. R. Schweizer, *ibid.*, p. 1934.

[5] J. Thiele and F. Günther, *Annalen*, 1906, **349**, 45.

[6] A. Oliverio and G. Castelfranchi, *Gazzetta*, 1950, **80**, 276.

[7] L. F. Fieser and M. I. Ardao, *J. Amer. Chem. Soc.*, 1956, **78**, 774.

[8] L. F. Fieser and M. Fieser, 'Advanced Organic Chemistry,' Reinhold Publishing Corp., New York, p. 855.

[9] H. W. Dorn, W. H. Warren, and J. L. Bullock, *J. Amer. Chem. Soc.*, 1939, **61**, 144.

[10] R. Fabinyi and T. Széki, *Ber.*, 1910, **43**, 2679.

[11] J. M. Blatchly, R. J. S. Green, J. F. W. McOmie, and J. B. Searle, following paper.

expected triacetate (4%) together with 1,4-diacetoxy-2,3,5-tribromobenzene (9%). With perchloric acid as catalyst only the diacetoxy-compound was formed (18%) while much of the quinone (44%) was recovered. The use of perchloric acid as catalyst for the Thiele acetylation of 2,5-dibromo- and 2,6-di-iodo-quinone also led to the formation of the corresponding hydroquinone diacetates as well as the expected triacetates. The di-iodo-quinone is the most sterically hindered of the halogeno-quinones which we have studied and, not surprisingly, it was the least reactive. Our qualitative results indicate that the order of reactivity of the 2,6-dihalogeno-quinones is I < Br < Cl and for the series of bromo-quinones, 2,3,5-tri- < 2,5-di- ≏ 2,3-di- < 2,6-di- < mono-bromo.

The quinones used in the present work were prepared in the following ways. 2-Iodoquinone was made from 2-iodophenol by Elbs persulphate oxidation [12] to the iodo-hydroquinone followed by oxidation with silver oxide in acetone. 2,3- and 2,5-Dibromoquinone were separated chromatographically, with some difficulty, from the mixture of quinones obtained by dibromination and subsequent oxidation of hydroquinone.[13] A similar, but new route, *via* dibromination followed by oxidation of 3-bromophenol, required the same difficult chromatographic separation of isomeric dibromo-quinones and presented no advantage over Bagli and Écuyer's method.[13] Tribromoquinone was made by the oxidation of tribromohydroquinone with silver oxide. It was also obtained by addition of hydrogen bromide to 2,5- and to 2,6-dibromoquinone, followed by oxidation, in 49 and 46% yield respectively.

2,6-Di-iodoquinone, made in three steps [14] from *p*-nitrophenol, has m.p. 180—181°. Metzeler [15] obtained a di-iodoquinone, m.p. 157—159° by the action of potassium iodate in dilute sulphuric acid on hydroquinone diacetate. Reduction of the quinone gave the corresponding hydroquinone, m.p. 142·5°, and thence the diacetate, m.p. 148°. We have repeated Metzeler's work and have obtained a product, m.p. 180—181°, which is identical with authentic 2,6-di-iodoquinone. The two derivatives made by Metzeler are likewise identical with authentic samples of 2,6-di-iodohydroquinone and its diacetate.

N.m.r. spectra (60 Mc./sec.), recorded in the Experimental section for most of the compounds described in this paper, confirm the structures assigned to the compounds on purely chemical grounds.

EXPERIMENTAL

Thiele Acetylation of 2,6-*Dichloroquinone*.—Boron trifluoride in acetic acid (40%; 1·52 ml.) was added to 2,6-dichloroquinone (1·52 g.) in acetic anhydride (15·2 ml.), and the mixture was kept at 45°. After 24 hr. it was poured into water and, after 6 hr., the precipitated solid was collected. Extraction of the solid with warm petroleum (b.p. 60—80°) (3 × 25 ml.) and evaporation of the extract gave unchanged quinone (0·2 g., 13%). The material (1·65 g., 62%) which was insoluble in petroleum was recrystallised from ethanol and gave 1,2,4-*triacetoxy*-3,5-*dichlorobenzene* (0·6 g.) as granules, m.p. 123·5—124° (Found: C, 45·1; H, 3·15. $C_{12}H_{10}Cl_2O_6$ requires C, 44·9; H, 3·1%).

3,5-*Dichloro*-1,2,4-*trimethoxybenzene*.—Sodium hydroxide (3·5 g.) in water (5 ml.) was added during 20 min. to a mixture of 1,2,4-triacetoxy-3,5-dichlorobenzene (0·6 g.), sodium dithionite (0·05 g.), methanol (4·2 ml.), and dimethyl sulphate (4·2 ml.) kept at 55—60°. After 30 min. more at 60°, water was added, then the mixture was cooled to 0° and the solid was collected. Two recrystallisations from petroleum (b.p. 60—80°) gave 3,5-dichloro-1,2,4-trimethoxybenzene (0·16 g., 38%), m.p. 55·5—57° (lit.,[6] 58°) (Found: C, 45·55; H, 4·1. Calc. for $C_9H_{10}Cl_2O_3$: C, 45·6; H, 4·25%).

Thiele Acetylation of 2-*Bromoquinone*.—(*a*) Bromoquinone (6·1 g.) in acetic anhydride (20 ml.) containing 40% boron trifluoride in acetic acid (1 ml.) was kept at 20° for 48 hr. 1,2,4-*Triacetoxy*-5-*bromobenzene* (4·5 g., 42%) was obtained as crystals (from ethanol), m.p. 116·5—117·5° (Found: C, 43·9; H, 3·5. $C_{12}H_{11}BrO_6$ requires C, 43·5; H, 3·35%).

(*b*) 72% Perchloric acid (0·5 ml.) was added to bromoquinone (9·3 g.) in acetic anhydride (50 ml.) and the mixture was kept at 20° for 8 hr. The product (4·6 g., 28%), m.p. 116—117°, was isolated and purified as in (*a*).

The triacetoxybromobenzene (1·16 g.) was hydrolysed and methylated (as described for the dichloro-compound) to give 5-bromo-1,2,4-trimethoxybenzene (0·45 g., 52%), which crystallised from petroleum (b.p. 60—80°) as cubes, m.p. 54—55·5°, mixed m.p. 54—55° with an authentic sample (Found: C, 44·0; H, 4·55. Calc. for $C_9H_{11}BrO_3$: C, 43·75; H, 4·5%).

Thiele Acetylation of 2-*Iodoquinone*.—A mixture of iodoquinone (0·57 g.), acetic anhydride (5 ml.), and 40% boron trifluoride in acetic acid (0·5 ml.) was kept at 25° for 4 hr. The product was twice recrystallised from ethanol and gave 1,2,4-*triacetoxy*-5-*iodobenzene* (0·32 g., 35%) as needles, m.p. 136—136·5° (Found: 38·3; H, 3·1; I, 33·8. $C_{12}H_{11}IO_6$ requires C, 38·1; H, 2·9; I, 33·6%).

The triacetoxy-compound, on hydrolysis and methylation, gave 5-iodo-1,2,4-trimethoxybenzene (49%), as needles from petroleum (b.p. 60—80°), m.p. 70—72° (lit.,[16] 70°) (Found: C, 36·65; H, 3·4. Calc. for $C_9H_{11}IO_3$: C, 36·8; H, 3·8%).

Thiele Acetylation of 2,6-*Dibromoquinone*.—(*a*) A mixture of 2,6-dibromoquinone (0·7 g.), acetic anhydride (5 ml.), and 40% boron trifluoride in acetic acid (0·4 ml.) was kept at 45° for 48 hr. The product gave 1,2,4-*triacetoxy*-3,5-*dibromobenzene* (0·35 g., 33%) as needles (from ethanol), m.p. 144—144·5° (Found: C, 35·45; H, 2·6. $C_{12}H_{10}Br_2O_6$ requires C, 35·15; H, 2·5%).

(*b*) A mixture of 2,6-dibromoquinone (8 g.), acetic anhydride (35 ml.), and 72% perchloric acid (0·85 ml.) was kept at 40° for 6 hr. The mixture yielded 1,2,4-triacetoxy-3,5-dibromobenzene (4·95 g., 40%), m.p. 144—144·5°.

The triacetoxy-compound (0·57 g.), on hydrolysis and methylation, gave 3,5-dibromo-1,2,4-trimethoxybenzene (0·25 g., 56%) (from methanol–water), m.p. 59·5—60°

[12] S. M. Sethna, *Chem. Rev.*, 1951, **49**, 91.
[13] J. F. Bagli and P. L. Écuyer, *Canad. J. Chem.*, 1961, **39**, 1037.
[14] R. Seifert, *J. prakt. Chem.*, 1883, **28**, 437; R. Block and G. Powell, *J. Amer. Chem. Soc.*, 1942, **64**, 1070.
[15] K. Metzeler, *Ber.*, 1888, **21**, 2554.
[16] H. Meerwein, P. Hofmann, and F. Schill, *J. prakt. Chem.*, 1940, **154**, 266.

(lit.,[10] 61°) (Found: C, 33·2; H, 3·1. Calc. for $C_9H_{10}Br_2O_3$: C, 33·2; H, 3·1%).

Thiele Acetylation of 2,5-Dibromoquinone.—(*a*) 2,5-Dibromoquinone (4 g.) in acetic anhydride (100 ml.) and 40% boron trifluoride in acetic acid (10 ml.) were stirred at 45° for 5 days. The mixture was chromatographed on a column of silica gel (150 g.). Elution with benzene–petroleum (b.p. 60—80°) (2 : 3) gave unchanged quinone (1·1 g., 28% recovery). Elution with benzene then gave 1,2,4-*triacetoxy*-3,6-*dibromobenzene* (3·0 g., 49%), which gave crystals (2·0 g.) (from ethanol), m.p. 132·5—133·5° (Found: C, 35·2; H, 2·5; Br, 39·0. $C_{12}H_{10}Br_2O_6$ requires C, 35·15; H, 2·5; Br, 39·0%).

(*b*) 2,5-Dibromoquinone (5·3 g.) in acetic anhydride (100 ml.) was treated dropwise with 72% perchloric acid (2 ml.) and stirred for 9 hr. at 50°. The mixture was poured into water and the oily product was collected in chloroform. The products were separated by chromatography as in (*a*). With benzene as eluant the first fraction contained 2,5-dibromohydroquinone diacetate (4·2 g., 60%) (from ethanol), m.p. 164—164·5°, mixed m.p. 163—165° with an authentic sample. The second fraction gave 1,2,4-triacetoxy-3,6-dibromobenzene (1·0 g., 12%) (from ethanol), m.p. 131·5—133·5°.

The triacetate was converted in the usual way into 3,6-*dibromo*-1,2,4-*trimethoxybenzene* (0·92 g., 77%) (from ethanol), m.p. 75—76° (Found: C, 33·2; H, 2·55. $C_9H_{10}Br_2O_3$ requires C, 33·2; H, 3·1%).

Thiele Acetylation of 2,3-Dibromoquinone.—A mixture of the quinone (0·35 g.) in acetic anhydride (2 ml.) and 40% boron trifluoride in acetic acid (0·1 ml.) was kept at 45° for 5 days. The product was crystallised twice from ethanol and gave 1,2,4-*triacetoxy*-5,6-*dibromobenzene* (0·17 g.), m.p. 112—113° (Found: C, 35·45; H, 2·6. $C_{12}H_{10}Br_2O_6$ requires C, 35·15; H, 2·5%). The ethanolic mother liquors were evaporated and the residue (0·23 g.) was chromatographed on a column of silica gel (25 g.). Elution with benzene–petroleum (b.p. 60—80°) (2 : 3) gave the quinone (0·1 g., 29% recovery). Benzene then eluted more (0·1 g.) of the triacetoxy-compound (total yield 47%).

Combined hydrolysis and methylation of the triacetoxy-compound gave 5,6-dibromo-1,2,4-trimethoxybenzene (59%) as needles, m.p. 99—100° (from aqueous acetic acid) (lit.,[9] 97°) (Found: C, 33·2; H, 2·9. Calc. for $C_9H_{10}Br_2O_3$: C, 33·2; H, 3·1%).

Thiele Acetylation of Tribromoquinone.—(*a*) The quinone (1·15 g.) in acetic anhydride (16 ml.) was treated with 72% perchloric acid (0·3 ml.) and kept at 50° for 12 hr. The product was chromatographed on silica gel (50 g.); elution with benzene–hexane (1 : 4) gave the quinone (0·5 g., 44% recovery). Elution with benzene then gave tribromohydroquinone diacetate (0·25 g., 18%) as needles from ethanol, m.p. and mixed m.p. 186—188°.

(*b*) The quinone (1·13 g.) in acetic anhydride (120 ml.) and 40% boron trifluoride in acetic acid (6 ml.) were kept at 45° for 30 days. The product was chromatographed on silica gel (60 g.) as in (*a*), except that increasing proportions of benzene to n-hexane were used as eluant. The first fraction gave tribromohydroquinone diacetate (0·12 g., 9%), m.p. 187—189°, mixed m.p. 186—188°. The second fraction gave tribromo-1,2,4-triacetoxybenzene (0·06 g., 4%) (from ethanol), m.p. 190—191° (lit.,[17] 189°) (Found: C, 29·7; H, 2·0; Br, 49·2. Calc. for $C_{12}H_9Br_3O_6$: C, 29·5; H, 1·9; Br, 49·0%).

(*c*) After a mixture of tribromoquinone (1 g.) in acetic acid (10 ml.) and 72% perchloric acid (0·4 ml.) had been kept at 45° for 21 days, dilution with water gave the starting quinone (0·92 g., 92% recovery). No product was obtained when the filtrate was extracted with ethyl acetate.

Thiele Acetylation of 2,6-Di-iodoquinone.—The quinone (2·5 g.) in acetic anhydride (30 ml.) and 72% perchloric acid (1 ml.) was kept at 45° for 20 hr. The product was digested with hot acetone–methanol (1 : 1) and the cooled solution was filtered to remove a tarry solid. The filtrate was concentrated and the first crop of solid gave 2,6-di-iodohydroquinone diacetate (1·5 g., 48%), m.p. 148—149° (from acetone) (lit.,[15] 148°) (Found: C, 27·1; H, 1·8. Calc. for $C_{10}H_8I_2O_4$: C, 26·9; H, 1·8%). The second crop gave 1,2,4-*triacetoxy*-3,5-*di-iodobenzene* (0·8 g., 23%), m.p. 148—149° (from methanol) (Found: C, 28·5; H, 2·1. $C_{12}H_{10}I_2O_6$ requires C, 28·6; H, 2·0%). A mixture of the di- and the tri-acetate had m.p. 135—143°.

When the quinone (4 g.) in acetic anhydride (30 ml.) and 40% boron trifluoride in acetic acid (2 ml.) was kept at 40—45° for 3 days it gave unchanged quinone (3·5 g.) and triacetate (0·55 g., 10%).

Iodoquinone.—Ammonium persulphate (12·6 g.) in water (50 ml.) was added dropwise to a stirred solution of *o*-iodophenol (10·1 g.) in 5N-sodium hydroxide (50 ml.) at 0°. The mixture was then allowed to warm to 20° and stirred at this temperature for 18 hr. It was acidified (Congo Red) with concentrated hydrochloric acid and the black tar was filtered off. The filtrate was extracted with ether then acidified with concentrated hydrochloric acid and heated on a water-bath for 1 hr. Extraction of the cooled solution with ether yielded a solid (3·75 g.), which gave iodohydroquinone (1·85 g., 14%) as cubic crystals from chloroform (charcoal), m.p. 115—117° (lit.,[18] 115—116°).

Freshly prepared silver oxide (2·3 g.) was added in portions during 5 min. to iodohydroquinone (1·2 g.) in acetone (10 ml.), at 5°. After being stirred for 10 min. more at 5°, the solution was filtered. The filtrate was evaporated, and the crude product (1·06 g., m.p. 62—63°) was sublimed at 40°/0·1 mm. to give iodoquinone as red cubes (1·0 g., 84%), m.p. 64—66° (lit.,[19] 63—64°) (Found: C, 30·9; H, 1·25. Calc. for $C_6H_3IO_2$: C, 30·8; H, 1·3%).

2,3,5-*Tribromoquinone.*—(*a*) Freshly prepared silver oxide (0·85 g.) was added in portions during 15 min. to a stirred solution of tribromohydroquinone (0·64 g.) in acetone (8 ml.). The solution was filtered and the filtrate yielded tribromoquinone (0·58 g., 91%) as golden-yellow plates, m.p. 155—156° (lit.,[13] 152—153°).

(*b*) A mixture of 2,5-dibromoquinone (5·8 g.) in acetic acid (20 ml.) and 45% hydrogen bromide in acetic acid (5·9 ml.) was kept for 12 hr., then a solution of anhydrous ferric chloride (26 ml. of a 60% w/v solution) was added. After 15 min. the mixture was diluted with water and the tribromoquinone was collected. The product (3·7 g., 49%) had m.p. 154—156° (from ethanol).

(*c*) When 2,6-dibromoquinone was treated with hydrogen bromide and then oxidised as in (*b*), tribromobenzoquinone was obtained (46%).

Acetylation of tribromohydroquinone gave *tribromohydroquinone diacetate*, m.p. 186—190° (Found: C, 28·0; H, 2·1; Br, 55·7. $C_{10}H_7Br_3O_4$ requires C, 27·9; H, 1·7; Br, 55·6%).

N.M.R. Spectra of Quinones.—(*a*) Benzoquinone: τ($CDCl_3$) 3·17. (*b*) Bromoquinone: τ($CDCl_3$) 2·85 (H-3, d), 3·35

[17] J. Thiele and K. Jaeger, *Ber.*, 1901, **34**, 2837.
[18] D. E. Kvalnes, *J. Amer. Chem. Soc.*, 1934, **56**, 667.
[19] P. R. Hammond, *J. Chem. Soc.*, 1964, 471.

(H-5, dd), and 3·08 (H-6, d), $J_{3,6}$ 0, $J_{3,5}$ 1·9, $J_{5,6}$ 10·2 c./sec. (*c*) Iodoquinone: τ($CDCl_3$) 2·55 (H-3, d), 3·33 (H-5, dd), and 3·20 (H-6, d), $J_{3,6}$ 0, $J_{3,5}$ 2·0, $J_{5,6}$ 9·9 c./sec. (*d*) 2,6-Dichloroquinone: τ($CDCl_3$) 3·17. (*e*) 2,3-Dibromoquinone: τ($CDCl_3$) 3·03. (*f*) 2,5-Dibromoquinone: τ($CDCl_3$) 2·56. (*g*) 2,6-Dibromoquinone: τ($CDCl_3$) 2·67. (*h*) 2,3,5-Tribromoquinone: τ($CDCl_3$) 2·65.

N.M.R. Spectra of 1,2,4-*Triacetoxybenzenes*.—(*a*) Parent compound: τ($CDCl_3$) 2·7—3·1 (H-3, H-5, H-6, complex m) and 7·75 (OAc). (*b*) 5-Bromo-: τ(CCl_4) 2·55 (H-6), 2·92 (H-3), 7·71 (OAc), and 7·81 (2 OAc), $J_{3,6}$ 0. (*c*) 5-Iodo-: τ($CDCl_3$) 2·58 (H-6), 3·15 (H-3), 7·73 (OAc), and 7·80 (2 OAc), $J_{3,6}$ 0. (*d*) 3,5-Dichloro-: τ($CDCl_3$) 2·93 (H-6) and 7·70, 7·75, and 7·80 (3 OAc). (*e*) 3,5-Dibromo-: τ($CDCl_3$) 2·50 (H-6), and 7·63, 7·68, and 7·76 (3 OAc). (*f*) 3,6-Dibromo-: τ(CCl_4) 2·75 (H-5) and 7·73 (3 OAc). (*g*) 5,6-Dibromo-: τ($CDCl_3$) 2·90 (H-3), 7·68 (2 OAc), and 7·77 (OAc). (*h*) 3,5,6-Tribromo-: τ($CDCl_3$) 7·65 (OAc) and 7·70 (2 OAc).

N.M.R. Spectra of 1,2,4-*Trimethoxybenzenes*.—(*a*) Parent compound: τ(no solvent) 3·45 (H-6, d), 3·63 (H-3, d), 3·83 (H-5, dd), 6·38 (2 OMe), and 6·43 (OMe), $J_{3,6}$ 0, $J_{3,5}$ 2·8, $J_{5,6}$ 8·7 c./sec. (*b*) 5-Bromo-: τ(CCl_4), 3·07 (H-6), 3·57 (H-3), 6·22 (2 OMe), and 6·25 (OMe), $J_{3,6}$ 0 c./sec. (*c*) 6-Bromo-: τ($CDCl_3$) 3·58 (H-5, d), 3·78 (H-3, d), 6·32 (OMe), 6·33 (OMe), and 6·40 (OMe), $J_{3,5}$ 2·8 c./sec. (*d*) 5-Iodo-: τ($CDCl_3$) 3·02 (H-6), 3·72 (H-3), 6·25 (OMe), 6·28 (OMe), and 6·30 (OMe), $J_{3,6}$ 0 c./sec. (*e*) 3,5-Dichloro-: τ($CDCl_3$) 3·37 (H-6) and 6·25 (3 OMe). (*f*) 3,5-Dibromo-: τ($CDCl_3$), 3·08 (H-6) and 6·22 (3 OMe). (*g*) 3,6-Dibromo-: τ($CDCl_3$), 3·31 (H-5), 6·18 (OMe), and 6·23 (2 OMe). (*h*) 5,6-Dibromo-: τ($CDCl_3$) 3·62 (H-3), 6·21 (OMe), 6·22 (OMe), and 6·30 (OMe).

We thank the Royal Society for a grant (to J. M. B.) through the Committee on Scientific Research in Schools.

[9/124 *Received, January 23rd,* 1969]