Medium-sized Cyclophanes. Part XIV.[1] An Aromatic Displacement Reaction in Veratrylic Compounds. Attempted Nitration and Halogenation of Cyclotriveratrylene (10,15-Dihydro-2,3,7,8,12,13-hexamethoxy-5*H*-tribenzo[*a*,*d*,*g*]cyclononene)

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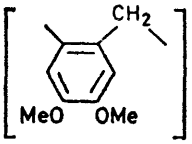
On nitration and halogenation cyclotriveratrylene did not give nuclear substituted derivatives but gave ring cleavage products in which a veratryl group was replaced by an electrophile. The cleavage reaction was shown to occur in a stepwise manner. Under controlled conditions *o*-dibenzylbenzenes such as (III)—(V), (X)—(XIII), and (XVI) were obtained in high yield and were further cleaved to diphenylmethane derivatives [(VI) and (XIV)] and veratrole derivatives [(VII), (VIII), and 4,5-dibromoveratrole]. Cleavage is facilitated because there is (a) high electron density *para* to a methoxy-group for electrophilic attack and (b) stabilization of the veratryl cation as a good leaving group. The tribenzocyclononene ring system is not inherently responsible for the cleavage.

THE acid-catalysed reaction of veratrole with formaldehyde or the condensation of veratryl alcohol has long been known to produce a high-melting, crystalline material. Robinson [2] considered it to be 2,3,6,7-tetramethoxy-9,10-dihydroanthracene (I; $n = 2$),[3]† while other workers gave a hexameric structure (I; $n = 6$).[5] Recently the correct trimeric structure (I; $n = 3$) was given to the compound known as cyclotriveratrylene (CTV) based on molecular weight determinations.[6-9] Formation of a cyclic tetramer (I; $n = 4$) has been reported.[6,10]



(I)

CTV exists in the crown conformation (II) [6-8,11,12] as does the parent ring system, all-*cis*-cyclonona-1,4,7-triene.[13] The AB quartet due to benzyl proton resonances does not change at 200° suggesting that the crown conformation is quite rigid.[11,12]

Inhibition of inversion in the nine-membered ring indicates the presence of conformational isomers and optical resolution might be possible with suitable chiral molecules. An elegant example by Lüttringhaus *et al.*[14] has shown that the monobenzyloxy-derivative is resolvable. We wished to obtain nuclear derivatives for optical resolution.‡ Under typical electrophilic conditions, however, cleavage products were obtained but no CTV derivatives were formed.[15]

Nitration.—Robinson [2] nitrated the compound which she considered to be (I; $n = 2$) and obtained 4,4′,5,5′-tetramethoxy-2,2′-dinitrodiphenylmethane (VI). The result which involves extrusion of one carbon fragment is perplexing although she believed the conversion to support her structural assignment. Similar studies were reported by Traverso.[16]

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† 2,3,6,7-Tetramethoxy-9,10-dihydroanthracene (I; $n = 2$) has been prepared.[4] See also ref. 5.

‡ There are six positions available for electrophilic substitution. Assuming each ring can accommodate one substituent and the second and third substitutions avoid the position facing this substituent, there will be one (±)-, one (±)- and one *meso*-, and two (±)-isomers for mono-, di-, and tri-substituted derivatives, respectively.

[1] Part XIII, T. Sato and K. Nishiyama, *J. Org. Chem.*, 1972, **37**, 3254.

[2] G. M. Robinson, *J. Chem. Soc.*, 1915, **107**, 267.

[3] C. A. Fletcher and M. T. Bogert, *J. Org. Chem.*, 1939, **4**, 71; G. Tsatsas, *Compt. Rend.*, 1951, **232**, 530; F. G. Jimenez, M. C. Perezamadov, and J. R. Alcayde, *Canad. J. Chem.*, 1969, **47**, 4489.

[4] P. W. Rabideau, *J. Org. Chem.*, 1971, **36**, 2723.

[5] A. Oliverio and C. Casinovi, *Ann. Chim.* (*Italy*), 1952, **42**, 168; 1956, **46**, 926. For another paper supporting a hexameric structure, see A. M. Liquori, F. Bertinotti, V. Carrelli, and A. M. Nardi, *Ricerca sci.*, 1952, **22**, 65.

[6] H. Erdtman, F. Haglid, and R. Ryhage, *Acta Chem. Scand.*, 1964, **18**, 1249.

[7] A. S. Lindsey, *Chem. and Ind.*, 1963, 823; *J. Chem. Soc.*, 1965, 1685.

[8] A. Goldup, A. B. Morrison, and G. W. Smith, *J. Chem. Soc.*, 1965, 3864.

[9] For other methods of preparation of CTV see T. Kametani, K. Yamaki, and K. Ogasawara, *Yakugaku Zasshi*, 1969, **89**, 638; B. Umezawa, O. Hoshino, H. Hara, K. Ohyama, S. Mitsubayashi, and J. Sakakibara, *Chem. Pharm. Bull. Japan*, 1969, **17**, 2240.

[10] J. D. White and B. D. Gesner, *Tetrahedron Letters*, 1968, 1591.

[11] B. Miller and B. D. Gesner, *Tetrahedron Letters*, 1965, 3351.

[12] R. C. Cookson, B. Halton, and I. D. R. Stevens, *J. Chem. Soc.* (*B*), 1968, 767.

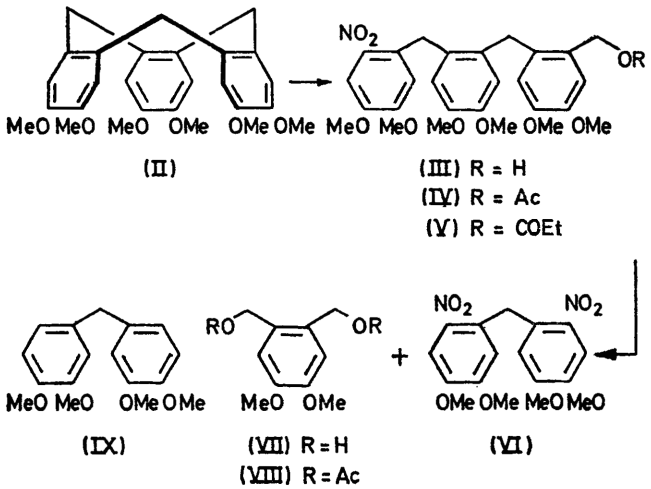
[13] P. Radlick and S. Winstein, *J. Amer. Chem. Soc.*, 1963, **85**, 344; K. G. Untch and R. J. Kurland, *ibid.*, p. 346.

[14] A. Lüttringhaus and K. C. Peters, *Angew. Chem.*, 1966, **78**, 603.

[15] Preliminary account, T. Sato, T. Akima, S. Akabori, H. Ochi, and K. Hata, *Tetrahedron Letters*, 1969, 1767.

[16] G. Traverso, *Gazzetta*, 1957, **87**, 67.

If these results are correct there must be a missing fraction containing one benzene ring. To isolate it and to obtain substituted CTV, if any, nitration was carried out under various reaction conditions. In order to have a homogeneous reaction and reagent control, nitration was studied using acyl nitrates [17] made from cupric nitrate–acetic anhydride (or propionic anhydride), nitric acid–acetic anhydride, or benzoyl chloride–silver nitrate.



(II)

(III) R = H
(IV) R = Ac
(V) R = COEt

(IX)

(VII) R = H
(VIII) R = Ac

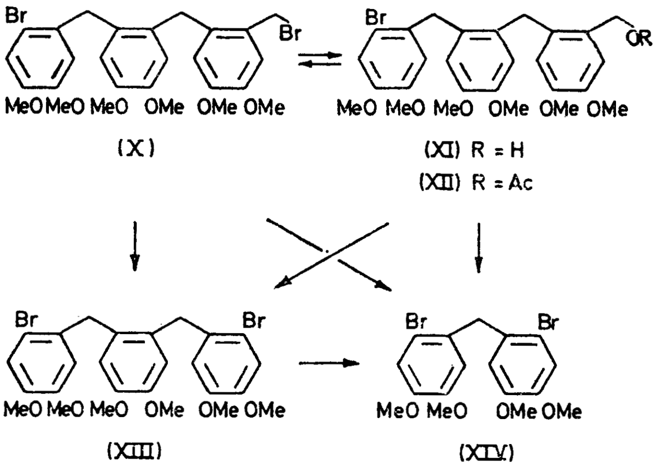
(VI)

With excess of acetyl nitrate, made from 1·5 equiv. or more of cupric nitrate, compound (VI) was produced in 82% yield. It was identical with that obtained by Robinson [2] and was characterized by the synthesis from the tetramethoxy-compound (IX).[5] 1,2-Bishydroxymethyl-4,5-dimethoxybenzene (VII) [18] was also isolated and identified by oxidation to 4,5-dimethoxyphthalide.[18] Compound (VI) was also obtained by treatment of CTV with nitric acid–acetic anhydride or with nitric acid. Compound (VII) was considered to be formed initially as the diacetate (VIII).

When CTV was treated with acetyl nitrate made from 1 mol. equiv. of cupric nitrate two new compounds were isolated. The nitroacetate (IV) was the initial product and was formed in an optimum yield of 76·5%. The yield of the nitro-alcohol (III), formed by hydrolysis of (IV), varied depending on the isolation conditions. Chromatography on neutral alumina minimized hydrolysis. Both (III) and (IV) were formed when CTV was treated with nitric acid–acetic anhydride. On further nitration the nitro-acetate (IV) was cleaved to a mixture of (VI) and (VII).

Halogenation.—The slow addition of bromine to CTV in acetic acid was difficult to control and gave a complex mixture of products. Accordingly we used bromine vapour for brominations. CTV in chloroform was exposed to a weighed quantity of bromine vapour overnight at room temperature. In this manner the bromo-alcohol (XI) was obtained in 66% yield. In addition, two dibromides (XIII) (10%) and (XIV) (14%) were isolated. The initial cleavage product is the dibromide (X), which is hydrolysed to (XI) during chromatography. This was proved by obtaining the bromo-acetate (XII) by treating the reaction mixture prior to chromatography with sodium acetate. On treatment with phosphorus tribromide compound (XII) gave (X), which on further contact with bromine vapour gave compounds (XIII) and (XIV). Likewise the bromo-alcohol (XI) gave compounds (XIII) (30%) and (XIV) (60%). The dibromide (XIII) gave (XIV) in a quantitative yield with bromine vapour.

In these brominations 4,5-dibromoveratrole was identified as the ultimate cleavage product by g.l.c. Neither (VII) nor (VIII) was identified since they were subject to further brominative cleavage.



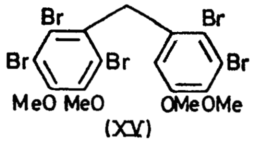
(X)

(XI) R = H
(XII) R = Ac

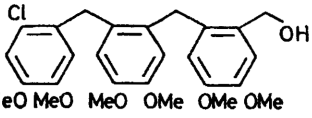
(XIII)

(XIV)

The dibromide (XIV) can be prepared from the tetramethoxy-compound (IX) on bromination. It was neither cleaved nor further brominated on treatment with bromine vapour. In the presence of an iron catalyst compound (IX) was converted into a mixture of polybromodiphenylmethanes from which the pentabromo-compound (XV) was isolated. Treatment of compound (XI) with 70% sulphuric acid produced CTV, whereas the same reaction of compound (III) resulted in the recovery of starting material. The formation of CTV from compound (XI) must involve replacement of bromine by a benzyl cation species. Chlorination of CTV in chloroform produced the chloro-alcohol (XVI).



(XV)



(XVI)

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[17] F. G. Bordwell and E. W. Garbisch, jun., *J. Amer. Chem. Soc.*, 1960, **82**, 3588; G. Bacharach, *ibid.*, 1927, **49**, 1522; K. I. H. Williams, S. E. Cremer, F. W. Kent, E. J. Sehm, and D. S. Tarbell, *ibid.*, 1960, **82**, 3982.

[18] J. H. Wood, M. A. Perry, and C. C. Tung, *J. Amer. Chem. Soc.*, 1950, **72**, 2989.

Products were characterized by analyses and by i.r., u.v., n.m.r., and mass spectra. The Table summarises the n.m.r. and u.v. data for representative compounds.

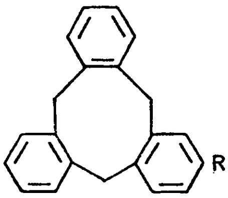
The question arises whether the cleavages are inherent in the rigid, overcrowded ring system of CTV, or can be ascribed to a veratryl structure. The mode of formation of double cleavage products such as (VII), which can be formed either by a stepwise manner or by simultaneous double cleavage is also interesting.

N.m.r. and u.v. spectral data

Compound	Chemical shift [δ (p.p.m.) from tetramethylsilane] [a]						
	Solvent	ArH	$ArCH_2Ar$	$ArCH_2Ar$	MeO	Others	$\lambda_{max.}$/nm (log ε) [b]
(VI)	$CDCl_3$	7·70 (2), 6·41 (2)		4·71 (2)	3·96 (6), 3·85 (6)		244 (4·41), 286 (4·07), 337 (4·07)
(IX)	$CDCl_3$	6·69 (4), 6·65 (2)		3·82 (2)	3·76 (6), 3·74 (6)		230 (4·19)+, 281 (3·80), 287 (3·73)+
	$CDCl_3$–C_6D_6 (1 : 1)	6·65 (4), 6·62 (2)		3·80 (2)	3·64 (6), 3·61 (6)		
(XIV)	$CDCl_3$	7·10 (2), 6·62 (2)		4·50 (2)	3·90 (6), 3·88 (6)		236 (4·34)+, 286 (3·85)
(XV)	$CDCl_3$	6·13		4·55 (2)	3·95 (3), 3·92 (3), 3·83 (3), 3·61 (3)		216 (4·91), 227 (4·59)+, 284 (3·34)+, 291 (3·36)
(III)	$CDCl_3$	7·57, 6·89, 6·54 (2) 6·46, 6·43	4·50 (2)	4·62 (2), 3·89 (2)	3·89 (3), 3·85 (3), 3·83 (3), 3·73 (3), 3·72 (6)	1·61 (OH)	233 (4·43)+, 284 (4·00), 341 (3·73)
	$CDCl_3$–C_6D_6 (1 : 1)	7·47, 6·80, 6·54, 6·50, 6·44, 6·31	4·38 (2)	4·25 (2), 3·83 (2)	3·66 (3), 3·58 (6), 3·55 (6), 3·45 (3)	1·30 (OH)	
(IV)	$CDCl_3$	7·52, 6·66, 6·53 (2), 6·49, 6·46	4·98 (2)	4·26 (2), 3·87 (2)	3·95 (3), 3·87 (3), 3·76 (6), 3·74 (6)	1·96 (Me)	236 (4·42), 284 (3·98), 343 (3·75)
	$CDCl_3$–C_6D_6 (1 : 1)	7·49, 6·79, 6·50 (2), 6·45, 6·33	4·97 (2)	4·26 (2), 3·87 (2)	3·63 (3), 3·57 (6), 3·55 (6), 3·45 (3)	1·80 (Me)	
(V)	$CDCl_3$–C_6D_6 (1 : 1)	7·46, 6·76, 6·46 (2), 6·42, 6·32	4·95 (2)	4·24 (2), 3·84 (2)	3·75 (3), 3·58 (6), 3·55 (6), 3·48 (3)	2·13, 1·00 (Et)	
(X)	$CDCl_3$	7·03, 6·85, 6·60, 6·55, 6·45 (2)	4·42 (2)	3·93 (4)	3·85 (3), 3·84 (3), 3·78 (3), 3·75 (3), 3·72 (3), 3·68 (3)		233 (4·47), 285 (4·01)
(XI)	$CDCl_3$	7·04, 6·96, 6·61, 6·53, 6·51, 6·43	4·53 (2)	3·93 (2), 3·88 (2)	3·88 (3), 3·86 (3), 3·79 (3), 3·75 (6), 3·69 (3)		233 (4·43), 285 (4·00)
(XII)	$CDCl_3$	7·05, 6·90, 6·58, 6·50 (2), 6·44	5·00 (2)	3·91 (2), 3·88 (2)	3·88 (3), 3·86 (3), 3·77 (3), 3·74 (6), 3·68 (3)	1·96 (Me)	235 (4·53), 285 (4·07)
	$CDCl_3$–C_6D_6 (1 : 1)	6·96, 6·83, 6·55, 6·48, 6·46, 6·39	4·97 (2)	3·92 (2), 3·87 (2)	3·75 (3), 3·65 (6), 3·63 (3) 3·62 (3), 3·56 (3)	1·86 (Me)	
(XIII)	$CDCl_3$	7·70 (2), 6·56 (2), 6·38 (2)		3·85 (2), 3·80 (2)	3·80 (6), 3·74 (6), 3·62 (6)		235 (4·46)+, 287 (4·03)
(XVI)	$CDCl_3$	6·92, 6·86, 6·60, 6·48 (2), 6·40	4·50 (2)	3·92 (2), 3·86 (2)	3·86 (3), 3·85 (3), 3·76 (3), 3·72 (6), 3·66 (3)	1·50 (OH)	

[a] With one exception (ethyl), all absorptions are singlets. Numbers in parentheses denote number of protons. Other signals are for one proton. [b] + = shoulder.

We have prepared the parent ring system of CTV, 10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (XVII; R = H),[19] which is also a crown-shaped molecule with a high temperature n.m.r. spectrum similar to that of CTV. On nitration it gave the mononitro-derivative (XVII; R = NO_2) with no indication of ring cleavage.[20] Thus, the tribenzocyclononene ring system itself is not susceptible to ring cleavage.*



(XVII)

Either acetyl nitrate or dinitrogen pentoxide is considered to be the reactive species in nitration with acetyl nitrate.[17,22] The predominant formation of the acetate (IV) in the nitration supports the participation of acetyl nitrate. This was confirmed by experiments using cupric nitrate–propionyl anhydride which produced the nitro-propionate (V). With dinitrogen pentoxide the formation of a nitro-nitrate is expected but it may be hydrolysed during work-up.

Electrophilic attack on an aromatic position bearing a substituent is called *ipso* attack and can subsequently lead to several different reaction paths.[23] In the present case displacement is facilitated since there is (a) high electron density *para* to a methoxy-group favouring *ipso* attack and (b) stabilization of the veratryl cation which serves as a good leaving group.

4,4′-Dimethoxydiphenylmethane gives substituted products in high yields on nitration † or on bromination [25]

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* After completion of our work Umezawa and his co-workers [21] carried out the bromination of CTV and reported the formation of (XI)—(XIII). They attributed the cleavages to ring strain.

† We obtained 4,4′-dimethoxy-3,3′-dinitrodiphenylmethane in 87·5% yield by nitration with cupric nitrate–acetic anhydride. See also ref. 24.

[19] T. Sato and K. Uno, *J.C.S. Chem. Comm.*, 1972, 579.

[20] Unpublished results.

[21] B. Umezawa, O. Hoshino, H. Hara, and S. Mitsubayashi, *J. Chem. Soc.* (*C*), 1970, 465.

[22] Protonated acyl nitrate is postulated, R. Taylor, *J. Chem. Soc.* (*B*), 1966, 727; A. A. Griswald and P. S. Starcher, *J. Org. Chem.*, 1966, **31**, 357.

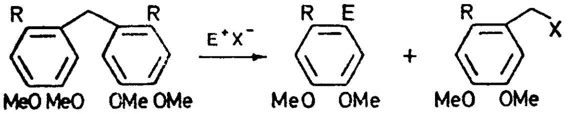
[23] C. L. Perrin and G. A. Skinner, *J. Amer. Chem. Soc.*, 1971, **93**, 3389, and references therein.

[24] K. Matsumura, *J. Amer. Chem. Soc.*, 1935, **57**, 128.

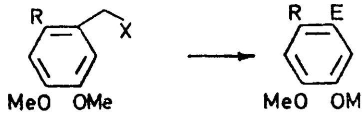
[25] E. M. Arnett and G. B. Klingensmith, *J. Amer. Chem. Soc.*, 1965, **87**, 1023. Ring bromination amounted to 99·8% and only 0·2% bromoanisole was detected.

with only a little debenzylation. By contrast, efficient cleavage occurred with methoxydiphenylmethanol.[25,26] The other reaction path constitutes the Stiles–Sisti aldehyde synthesis.[27] For effective debenzylation a veratryl structure appears to be necessary.

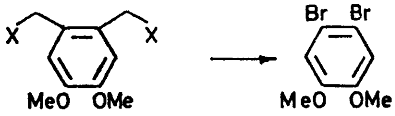
In the present studies three types of cleavages (1)—(3) have been noticed. In types (1)—(3) R represents a veratrylic residue and X stands for acetoxy, halogen, or others. Nitration, bromination, and chlorination cause the reactions shown in equation (1), whereas the reactions in equations (2) and (3) occurred only in halogenation. Extensive cleavage as in types (2) and (3) has been observed during the chlorination of lignin models[28] and *p*-hydroxybenzyl alcohol.[29]



(1)



(2)



(3)

EXPERIMENTAL

M.p.s are uncorrected. T.l.c. was carried out using Wako gel B-5. For column chromatography Woelm neutral alumina (activity grade II or III) or Florisil was employed. N.m.r. spectra were recorded on a Hitachi R-20A or a Varian HA-100 spectrometer using tetramethylsilane as internal reference. U.v. and i.r. spectra were recorded on Hitachi EPS-3T and EPI-G2 spectrometers, respectively. Mass spectra were run on a Hitachi RMU-6 machine.

Cyclotriveratrylene (*CTV*).—Several modified procedures have been reported for the synthesis of CTV.[2,3,5,9,10] We used a simplified procedure. To concentrated HCl (200 ml) and paraformaldehyde (6·5 g, 0·22 mol) veratrole (25 g, 0·18 mol) was added with stirring. The mixture warmed and became viscous. After being left for 3 h at room temperature it was extracted with benzene. The extract was washed (10% Na_2CO_3) and concentrated. CTV was obtained in 45% yield as needles, m.p. 228—230° (from benzene).

Nitration of CTV with Excess of Reagent.—4,4′,5,5′-*Tetramethoxy*-2,2′-*dinitrodiphenylmethane* (VI) *and* 1,2-*bishydroxymethyl* 4,5-*dimethoxybenzene* (VII). Acetic anhydride (20 ml) and cupric nitrate trihydrate (1·5 g, 6·3 mmol) were stirred at room temperature until a greenish blue precipitate of cupric acetate appeared. To the acetyl nitrate solution CTV (1·8 g, 4·0 mmol) was added and the mixture was poured into water and extracted with benzene. The extract was washed (aq. $NaHCO_3$), dried ($MgSO_4$), and concentrated. Chromatography on alumina using benzene as eluant gave the dinitro-compound (VI) as yellow crystals (1·23 g, 82%), m.p. 179—180° (from CCl_4) (lit.,[2] 183°). It was also obtained by the nitration of compound (IX),[5] *m*/*e* 378; $\nu_{max.}$ (KBr) 1515 and 1328 cm^{-1} (Found: C, 54·1; H, 4·75; N, 7·4. Calc. for $C_{17}H_{18}N_2O_8$: C, 53·95; H, 4·8; N, 7·4%).

On further elution the diol (VII) was obtained as pale yellow needles (252 mg, 25·5%), m.p. 107—110·5° (from benzene–CCl_4) (lit.,[18] 114—115°), $\nu_{max.}$ (KBr) 3520 and 1100 cm^{-1} (Found: C, 60·75; H, 7·1. Calc. for $C_{10}H_{14}O_4$: C, 60·6; H, 7·1%).

Compound (VII) was identified by converting it into 4,5-dimethoxyphthalide.[18] The minor products (III) (3·6%) and (IV) (7·5%) were also isolated. Both compounds (VI) and (VII) were formed as the major products when an excess of nitrating agent was used. For example, (VI) was formed in 80% yield with HNO_3–acetic anhydride.

Nitration under Controlled Conditions.—4-(4,5-*Dimethoxy*-2-*nitrobenzyl*)-5-(2-*hydroxymethyl*-4,5-*dimethoxy*-2-*nitrobenzyl*)-1,2-*dimethoxybenzene* (III) *and its acetate* (IV). To an acetyl nitrate solution from acetic anhydride (20 ml) and cupric nitrate trihydrate (0·5 g, 4 mmol), CTV (1·8 g, 4 mmol) in acetic acid (10 ml) was added. After stirring for 30 min at 50° the mixture was poured into water. Compound (IV) was obtained as pale yellow crystals (1·7 g, 76·5%), m.p. 119—121° (from CCl_4), $\nu_{max.}$ (KBr pellet) 1740, 1510, and 1330 cm^{-1} (Found: C, 62·6; H, 5·9; N, 2·85. $C_{29}H_{33}NO_{10}$ requires C, 62·7; H, 6·0; N, 2·5%). The reaction was repeated under similar conditions and the mixture was examined by t.l.c. and column chromatography. By this procedure, the starting material, (VI) and (III) were isolated. The *nitro-alcohol* (III) was obtained as a pale yellow powder, m.p. 124—124·5°, in variable yields up to 21·5%. Compound (III) was formed by the hydrolysis of (IV). With alumina column chromatography extensive hydrolysis occurred, which was minimized when neutral alumina (Woelm activity II or III) was used. Florisil was the second choice. Compound (III) had $\nu_{max.}$ (KBr) 3500, 1510, and 1330 cm^{-1} (Found: C, 63·3; H, 5·9; N, 2·8. $C_{27}H_{31}NO_9$ requires C, 63·15; H, 6·1; N, 2·75%).

Nitration with Cupric Nitrate–Propionyl Anhydride.—A similar reaction using propionyl anhydride in place of acetic anhydride produced the nitro-propionate (V) $\nu_{max.}$ (KBr pellet) 1735 and 1520 cm^{-1}.

Nitration with Benzoyl Nitrate.—A solution of CTV (1·8 g, 4 mmol) in chloroform (35 ml) was added to benzoyl nitrate (12 mmol) in chloroform (12 ml) in an ice-bath. After 15 min stirring it was left for 17 h. By the usual work-up compound (III) (16·5%) and recovered CTV (10·5%) were obtained. A small amount of compound (VI) was also isolated.

Bromination of CTV.—In a closed vessel equipped with a pressure equalizing device CTV (4·5 g, 10 mmol) in chloroform (50 ml) was exposed to bromine vapour (1·65 g, 10 mmol) for 24 h at room temperature. After the solution was poured into water and treated as usual the product was passed through alumina. From the eluate compound (XIV) (0·25 g, 14%), m.p. 97·5—98·5° (from CCl_4), was isolated. It was identical with the compound prepared from (IX) by bromination (Found: C, 46·1; H, 4·35; Br, 35·7. $C_{17}H_{18}BrO_4$ requires C, 45·8; H, 4·05; Br, 35·8%).

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[26] E. M. Arnett and G. B. Klingensmith, *J. Amer. Chem. Soc.*, 1965, **87**, 1038.

[27] M. Stiles and A. G. Sisti, *J. Org. Chem.*, 1960, **25**, 1691.

[28] J. B. van Buren and C. W. Dence, *Tappi*, 1961, **44**, 459; 1967, **50**, 553.

[29] K. V. Sarkanen and C. W. Dence, *J. Org. Chem.*, 1960, **25**, 715.

Further elution gave 4-(2-*bromo*-4,5-*dimethoxybenzyl*)-5-(2-*hydroxymethyl*-4,5-*dimethoxybenzyl*)-1,2-*dimethoxybenzene* (XI) (66%), m.p. 143—144° (from CCl_4), $\nu_{max.}$ (KBr pellet) 3500 and 1095 cm^{-1} (Found: C, 58·95; H, 5·75; Br, 14·5. $C_{27}H_{31}BrO_7$ requires C, 59·25; H, 5·7; Br, 14·6%).

On acetylation with acetic anhydride compound (XI) gave the acetate (XII). 4,5-Dibromoveratrole was identified by gas chromatography.

Bromination of Compound (XI).—By treatment of CTV (1·6 g, 3 mmol) in chloroform (30 ml) using bromine (0·9 g, 3 mmol) as above for 24 h, 4,5-*bis*-(2-*bromo*-4,5-*dimethoxybenzyl*)-1,2-*dimethoxybenzene* (XIII), m.p. 134·5—135·5°, was obtained in 30% yield, *m/e* 594 (Found: C, 52·45; H, 4·65; Br, 26·6. $C_{26}H_{32}Br_2O_6$ requires C, 52·0; H, 5·35; Br, 26·6%). Compound (XIV) was obtained in 6% yield.

Bromination of Compound (XIII).—Bromination of compound (XIII) as above gave compound (XIV) (90%).

Bromination of Compound (XIV).—2,2′,3,3′,6-*Pentabromo*-4,4′,5,5′-*tetramethoxydiphenylmethane* (XV). Compound (XIV) was found to be stable towards further bromination when in contact with bromine vapour alone. In the presence of iron powder compound (XIV) was brominated in CCl_4 at 65—70°. Among other products compound (XV) was obtained in 35% yield, m.p. 144—146° (Found: C, 29·95; H, 2·3. $C_{17}H_{15}Br_5O_4$ requires C, 29·9; H, 2·2%).

Chlorination of CTV.—4-(2-*Chloro*-4,5-*dimethoxybenzyl*)-5-(2-*hydroxymethyl*-4,5-*dimethoxybenzyl*)-1,2-*dimethoxybenzene* (XVI). Chlorine (4 mmol) in chloroform (4 ml) was added to CTV (1·8 g, 4 mmol) in chloroform at room temperature. Stirring was continued for 30 min. Among other products, compound (XVI) was isolated, m.p. 144°, $\nu_{max.}$ (KBr) 3510 and 1100 cm^{-1} (Found: C, 63·5; H,6·05; Cl, 7·25. $C_{27}H_{31}ClO_7$ requires C, 64·45; H, 6·2; Cl,7·05%).

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