Acta Chemica Scandinavica B 29 (1975) 124—132

Derivatives of Glutacondialdehyde. 2.* Ring Opening of 3-Methyl- and 3-Methoxypyridine. Preparation of 2- and 4-Substituted Glutacondialdehyde Derivatives. The Structure of the Glutacondialdehyde Bis-diacetal

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Ring opening of 3-methyl- and 3-methoxypyridinium-1-sulfonate and benzoylation of the salts obtained were found to occur *via* a specific reaction, yielding only 4-methyl- and 4-methoxy-5-hydroxy-*trans*-2,*trans*-4-pentadienal benzoate. A 1:1 mixture of the 2-methyl-5-hydroxy-*trans*-2,*trans*-4-pentadienal benzoate and the isomeric 4-methyl-benzoate was obtained by hydrolysis and benzoylation of 1,1,3,5,5-pentaethoxy-2-methylpentane. Bromination followed by benzoylation of the glutacondialdehyde sodium salt yielded the 2-bromo benzoate, which was also obtained from the glutacondialdehyde benzoate by bromination.

All double bonds in these derivatives were found to have the *trans* configuration, as well as the double bond in the bisdiacetal of glutacondialdehyde. This has been confirmed by microwave broad band spectroscopy in the vapour phase.

The preparation of 1,1,3,5,5-pentamethoxypentane directly from the sodium salt of glutacondialdehyde is reported.

In a previously paper [1] we described the final structure determination, mainly by ^{1}H NMR, of the sodium salt of glutacondialdehyde (IVa). Glutacondialdehyde in solution,[2] $\tau_{1/2}$ in ether < 10 min at room temperature, polymerises easily.

In the course of that work, we found the potentially quite useful ring opening of pyridines to glutacondialdehyde had never been subjected to much scrutiny,[3] except in the case of pyridine itself.[4] Furthermore, simple substituted glutacondialdehydes are not well examined, and since such dialdehydes offer many synthetic applications, we decided to examine further ring openings of substituted pyridines as well as the chemistry of the corresponding glutacondialdehydes.

RESULTS

Our first approach was to examine the ring opening reaction of a series of substituted pyridines, namely 3-methyl-, 4-methyl-, 3,5-dimethyl-, 4-*tert*-butyl-, and 3-methoxypyridine, under the reaction conditions where the two step reaction led to a high yield of ring opening product from pyridine itself.[4]

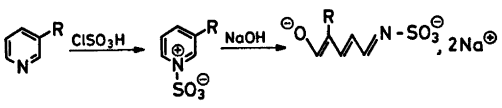
4-Methylpyridine yielded only tarry materials. 3,5-Dimethyl- and 4-*tert*-butylpyridine reverted to the parent amine, while 3-methyl- and 3-methoxypyridine nicely ring opened, to give the unstable yellow disodium salts IIIb and IIId, respectively, in excellent yield. However, attempts to transform compounds IIIb and IIId into the sodium salts of the corresponding glutacondialdehydes failed.*

Benzoylation of compounds IIIb and IIId led to the formation of the mono-benzoylated derivatives, VIb and VId, respectively. VIb in

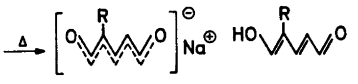
* Part 1, see Ref. 1.

** Section on microwave spectra only.

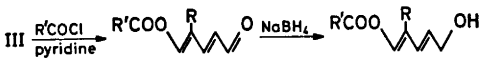
* See later in the discussion for the transformation of I to IV.



I II III



IV V

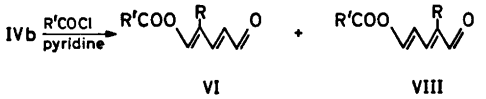


VI VII

a: R=H , R'=C_6H_5
b: R=CH_3 , R'=C_6H_5
c: R=CH_3 , R'=C_6D_5
d: R=OCH_3 , R'=C_6H_5
e: R=OCH_3 , R'=C_6D_5

turn was reduced to the expected [1] alcohol VIIb with sodium borohydride.

Yanovskaya and Kucherov [5] reported the preparation of a benzoyl derivative of Vb; but apparently were not sure of the position of the methyl group. Therefore we repeated their experiments, and found that a 1:1 mixture of the isomers VIb and VIIIb was obtained:

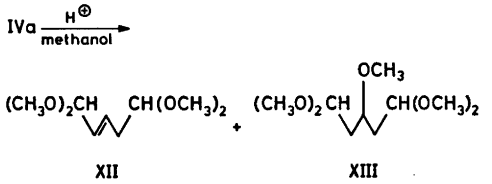


VI VIII

b: R=CH_3 , R'=C_6H_5
c: R=CH_3 , R'=C_6D_5

Furthermore, we reinvestigated the bromination of IVa and of the benzoyl derivative VIa. Upon bromination each yielded a mono bromo derivative, to which we assign structures IX and X, respectively. Baumgarten [4a] previously reported a lower melting point for X, for which he assumed the bromo atom to be substituted at the 4-position. It should be noted that IX was isolated as the benzoyl derivative X. Sodium borohydride reduction of X gave XI.

As a part of the structure determination we also reinvestigated the preparation of the tetramethyl acetal of IVa, previously described by Merländer.[6] We found that treatment of IVa with methanol led to the reported tetramethyl acetal XII, and as a higher boiling fraction the very stable 1,1,3,5,5-pentamethoxypentane (XIII).

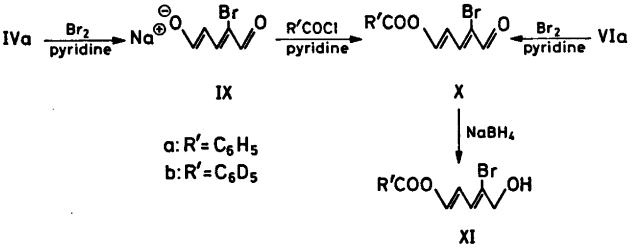


XII XIII

Structural assignments. All of the above described compounds showed the expected elemental composition. The ultraviolet and infrared spectra (Tab. 1) all are in good agreement with the assignments. However, the main evidence was found in the ^1H NMR spectra (Table 2).

The all-*trans* configuration is inferred from the IR-absorptions at 935 – 975 cm^{-1}; (see Ref. 1). The ^1H NMR spectra of all compounds,* as seen from the table, had the coupling constant $J_{2,3}=15$ Hz which is only compatible with a *trans* configuration. Similarly the coupling constant $J_{4,5}=11-12$ Hz is again consistent with a *trans* configuration. The location of the

* The numbering of the glutacondialdehyde derivatives has been defined in Ref. 1 as
RCOO–CH=CH–CH=CH–CHO.
5 4 3 2 1



IX X XI

a: R'=C_6H_5
b: R'=C_6D_5

Table 1. Spectral properties of glutacondialdehyde derivatives.

Compound	No.	UV absorption spectra in abs. ethanol		IR absorption spectra in KBr		
				OH	CHO	*trans* C=C
		λ_{max} mμ	log ε	cm^{-1}	cm^{-1}	cm^{-1}
5-Hydroxy-*trans*-2,*trans*-4-pentadienal benzoate						
2-methyl-	VIIIb	237 289	4.06 4.55		2580 2720 2815	936
4-methyl-	VIb	233 288	3.99 4.49		2700 2735 2810	970
2-bromo-	Xa	237 300	4.02 4.49		2842	948
5-Hydroxy-*trans*-2,*trans*-4-pentadienal hexadeuteriobenzoate						
2-methyl-	VIIIc	236 289	3.94 4.54		2690 2790 2890	945
4-methyl-	VIc	232 289	3.80 4.43		2700 2735 2815	970
2-bromo-	Xb	239 303	4.04 4.46		2845	948
trans-2,*trans*-4-Pentadiene-1,5-diol-5-benzoate						
4-methyl	VIIb	229 267	4.45 4.21	3340		965
2-bromo-	XIa	233 269	4.31 4.27	3250		938
trans-2,*trans*-4-Pentadiene-1,5-diol-5-hexadeuteriobenzoate						
2-bromo-	XIb	233 268	4.22 4.30	3400		937
1,1,5,5-Tetramethoxy-*trans*-2-pentene						
	XII					975
5-Hydroxy-*trans*-2,*trans*-4-pentadienal benzoate						
4-methoxy-	VId				2700 2735 2815	970
5-Hydroxy-*trans*-2,*trans*-4-pentadienal hexadeuteriobenzoate						
4-methoxy-	VIe				2700 2735 2815	970

substituents follows from the splitting of the individual signals, and from the chemical shifts.

The steric structure, *i.e. trans* or *cis*, of IIIa, IIIb or IIId was shown to be *trans* in the case of IIId, the ^1H NMR spectrum of which was found to be similar to the spectrum found for IVa.[1] The ^1H NMR spectra of IIIa and IIIb were not obtained due to the insolubility of these salts, but as their UV and IR spectra [12] closely resembled that of IIId, these salts must

also be assigned the *trans* structure.

All the assignments described above correspond to similar results for some amino derivatives of the glutacondialdehyde type reported by Dillon and Lewis,[7] where $J_{trans} = 11 - 15$ Hz, Schibe and Jutz [8] $J_{trans} = 11.8 - 12.7$ Hz and by Marvell, Li and Paik [9] $J_{trans} = 12$ Hz.

MICROWAVE SPECTRA

A low-resolution microwave-spectrum of 5-hydroxy-*trans*-2,*trans*-4-pentadienal acetate[1] has been recorded at a vapour pressure of 0.03 mmHg on a Hewlett-Packart MRR-spectrometer.

The spectrum (Fig. 1) consists of unresolved "bands" approximately 100 MHz wide and 703 MHz apart, with no appreciable fine structure. (30 000 MHz correspond to 1 cm^{-1} on the more

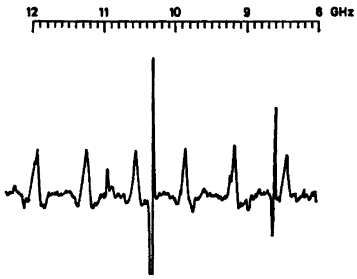


Fig. 1. Microwave spectrum of 5-hydroxy-*trans*-2,*trans*-4-pentadienal acetate.

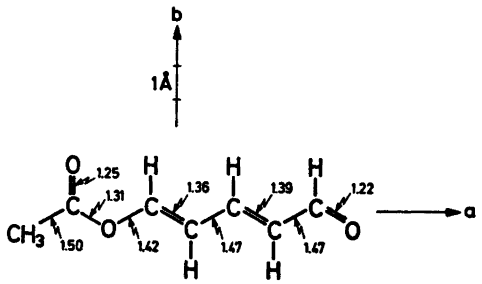


Fig. 2. 5-Hydroxy-*trans*-2,*trans*-4-pentadienal etacate.

familiar wave number scale). These findings indicate that the molecule is very close to the limit, where the two largest moments of intertia are equal (the prolate limit). They also indicate that the molecule possesses a dipole component in the direction of the axis of smallest moment of inertia. In Fig. 2 this axis is designated by *a*, while the axes of largest moments of inertia are designated by *b* and *c* (not shown in the figure). Also indicated on the figure are a set of reasonable geometrical parameters which give a good description of the spectrum in the following sense:

The spectrum reflects the free rotation of the molecule, and it is described to a good approximation by the formula:

$$\nu_{J \to J+1} = 2B^{+}(J+1)$$

with B^{+} expressed in terms of the moments of inertia as follows:

$$B^{+} = f(1/I_b + 1/I_c)$$

with ν in MHz and I_b, I_c in u$Å^2$, $f = 505\,376/2$. J is the rotational quantum number, which may be found from the spectrum by dividing the spacing between two peaks ($2B^{+}$) into the frequency of the lower of the two peaks.

The moments of inertia of the model of Fig. 2 are $I_b = 1449$ u$Å^2$ and $I_c = 1508$ u$Å^2$ giving $2B^{+} = 684$ MHz, in good agreement with the observed value of 703 MHz.

The conformation shown in Fig. 2, and the conformation obtained by rotating the acetyl group by 180°, must have almost the same moments of inertia, therefore the microwave spectra can say nothing conclusive in this regard. However, it is well known [10] that esters in general favour a conformation where C=O and the ester alkyl group are *cis*. We therefore presume that the conformation giving rise to the spectrum is the one shown in Fig. 2.

DISCUSSION

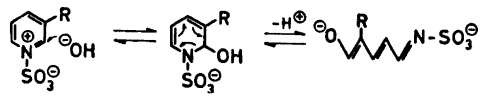
The benzoylation of III thus gives only the 4-substituted isomer VI, without a trace of the 2-substituted isomer. This highly specific reaction is mirrored in the bromination reactions of IVa and VIa, which reactions yielded only Xa. Thus the opening of the pyridine ring seems to occur as follows:

Table 2. Nuclear magnetic resonance parameters.[a]

Compound[b]	Protons at carbon number C_1	C_2	C_3	C_4	C_5	Other protons
VIIIb	0.59, s, 1 H	–	3.10, d,m, *J* 11.4, 1 H	3.45, t, *J* 11.4, 1 H	2.02, d, *J* 11.4, 1 H	8.11, s, 3 H, methyl H; 1.85–2.05, m, 2H and 2.44–2.68, m, 3H, aromatic H
VIb	0.36, d, *J* 7.5 1 H	3.74, d,d, *J* 7.5, J 15.0, 1H	2.74, d, *J* 15.0, 1 H	–	2.06, m, *J* 1.5, 1 H	1.75–1.92, m, 2H and 2.53–2.84, m, 3H aromatic H; 8.00, d *J* 1.5, 3 H methyl H
Xa	0.75, s, 1 H	–	2.45, d, *J* 10.5, 1 H	3.22, d,d, *J* 12.0, *J* 10.5, 1 H	1.80, d, *J* 12.0, 1 H	1.75–2.50, m 5 H, aromatic H
VIIIc	0.58, s, 1 H	–	3.10, d,m, *J* 11.4, 1 H	3.45, t, *J* 11.4, 1 H	2.02, d, *J* 11.4, 1 H	8.11, s, 3 H methyl H
VIc	0.36, d, *J* 7.5, 1 H	3.74, d,d, *J* 7.5 *J* 15.0, 1 H	2.75, d, *J* 15.0, 1 H	–	2.07, m, *J* 1.5 1 H	7.96, d, *J* 1.5, 3 H, methyl H
Xb	0.78, s, 1 H	–	2.48, d, *J* 10.9, 1 H	3.25, d,d, *J* 11.6, *J* 10.9, 1 H	1.80, d, *J* 11.6, 1 H	–
VIIb	5.80, d, *J* 5.3, 2 H	4.21, d,t, *J* 15.0 5.3, 1 H	3.72, d, *J* 15.0, 1 H	–	*ca.* 2.55, m, *J* 1.5, 1 H	8.05, d, *J* 1.5, 3 H, methyl H; s, 7.75, 1 H, OH; 1.91–2.08, m 2 H and 2.45–2.78, m, 3 H, aromatic H

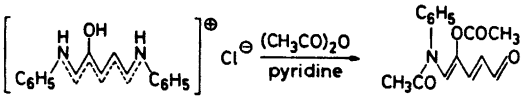
XIa	5.71, s, 2 H	–	3.31–3.80, m, *J* 12.0, *J* 10.5		2.24, d, *J* 10.5, 1 H	1.85–2.84, m, 5 H, aromatic H; 7.78, s, 1 H, OH
XIb	5.71, s, 2 H	–	*ca.* 3.53, m, *J* 10.5		2.24, d, *J* 10.5, 1 H	7.78, s, 1 H, OH
XII	5.24,d, *J* 5.4, 1 H	4.51, d,d, *J* 5.4, *J* 15.0 1 H	4.08, d,d, *J* 6.0, *J* 15.0 1 H	7.56, t, *J* 6.0, 2 H	5.56, t, *J* 6.0, 1 H	6.64, s,12 H, methyl H
XIII	5.50, t, *J* 6.0, 2 H	8.29, t, *J* 6.0, 4 H	6.78, t, *J* 6.0, 1 H	See C_2	See C_1	6.62, s, 3 H, 6.70, s, 12 H, methyl H
VId	0.40, d, *J* 7.5, 1 H	3.56, d,d, *J* 7.5, *J* 15.0, 1 H	3.13, d, *J* 15.0, 1 H	–	2.46, s, 1 H	1.80–1.98, m, 2 H and 2.33–2.55, m, 3 H, aromatic H, 5.98, s, 3 H, OCH_3
VIe	0.40, d, *J* 7.5, 1 H	3.56, d,d, *J* 7.5, *J* 15.0, 1 H	3.13, d, *J* 15.0, 1 H	–	2.46, s, 1 H	5.98, s, 3 H, OCH_3
IIId [c]	2.10, d, *J* 10.5, 1 H	4.72, d,d, *J* 10.5, *J* 13.5, 1 H	3.52, d, *J* 13.4 1 H	–	2.12, s, 1 H	6.53, s, 3 H, OCH_3

[a] All spectra were recorded at 60 Mc/s with TMS as internal reference. Chemical shifts are in τ-units, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, d,d = doublet of doublets, d,t = doublet of triplets, t,t = triplet of triplets, and the coupling constants are given in Hz.
[b] Deuteriochloroform was used as solvent, in the case of no remarks. [c] In hexadeuteriodimethyl sulfoxide.



The proposed reaction scheme explains the position for attack at the pyridine ring where R = CH_3 or OCH_3. The steps seem to be reversible, *e.g.* hydrolyses of the unstable salt III regenerates the parent pyridine.

A similar specific acylation reaction of a related glutacondialdehyde derivative has been reported by Dillon and Lewis.[7] They found that acetylation of the so-called Stenhouse salts in pyridine yielded exclusively one isomer, while the same reaction carried out in water gave a mixture of the two possible isomers.



a "Stenhouse salt"

These results suggest that acylation reactions performed in pyridine are specific for the glutacondialdehyde derivatives with an imide function such as in III or in the Stenhouse salts. However, in the case of the glutacondialdehyde sodium salts IVa and IVb acylation of the enol form resonance structure was non specific and the two possible isomers were obtained in a 1:1 ratio. This investigation will be continued with other pyridines as well as substituted glutacondialdehydes.

EXPERIMENTAL

Microanalyses were carried out in the Microanalytical Department of the University of Copenhagen by Mr. Preben Hansen. Melting points (uncorrected) were determined on a Büchi melting point apparatus.

Infrared spectra were recorded on a Perkin Elmer Model 457 grating infrared spectrophotometer. Ultraviolet spectra were recorded on a Beckman ACTA III spectrophotometer by Mrs. Bodil Kroneder. Proton magnetic resonance spectra were recorded on a Jeol C-60HL NMR spectrometer by Mrs. Eva Heyn Olsen, who also assisted with some of the preparations.

TLC, thin layer chromatography, and PTLC, preparative layer chromatography, were performed on silica gel with benzene as eluent.

Gas chromatography was carried out on a Varian Autoprep Gas Chromatograph.

5-Hydroxy-trans-*2*,trans-*4-pentadienal benzoate (VIa)*. The previously reported [1] benzoyl derivative VIa was prepared as described for VId. Thus 4.0 g of IIIa in 30 ml of pyridine and 2.0 ml of benzoyl chloride yielded 0.54 g (11 %) of VIa.

3-Methyl pyridinium-1-sulfonate (IIb).[11] 3-Methyl pyridine (12.4 g) dissolved in 40.0 ml of chloroform was cooled to −20 °C, whereupon chlorosulfonic acid (4.36 ml) was added slowly during 75 min while the temperature was maintained at −5 to 0 °C. Stirring was continued for 90 min at −20 °C. The product was filtered, washed with pentane (20 ml) and dried at 20 °C/1 mmHg. Yield of IIb as white crystals, m.p. 140−148 °C was 8.2 g (44 %). (Found: C 38.60; H 4.64; N 7.51; S 16.25. Calc. for $C_6H_7NO_3S.3/4H_2O$: C 38.60; H 4.59; N 7.50; S 17.17).

Ring opening of 3-methyl pyridinium-1-sulfonate (IIb) to give IIIb. Disodium 4-methyl-5-oxido-trans-*2*,trans-*4-pentadienylidenamin*-N-*sulfonate (IIIb)*. IIb (21 g) was cooled to −15 °C. To these crystals was added during 5 min with stirring a solution of sodium hydroxide (10 g) dissolved in 68 ml of water previously cooled to −20 °C. Stirring was continued at this temperature for 30 min. The suspension turned bright yellow and stirring was continued at room temperature for 2½ h. The product was filtered and washed with methanol to yield 21 g (74 %) disodium salt IIIb as bright yellow crystals (UV and IR nearly identical [12] with the corresponding salt [2] obtained from the unsubstituted pyridine). (Found: C 28.85; H 3.68; N 5.37; S 12.73. Calc. for $C_6H_6Na_2NSO_4.H_2O$: C 28.58; H. 3.20; N 5.56; S 12.71).

3-Methoxy pyridinium-1-sulfonate (IId). The above described method was used. Thus 3-methoxy pyridine (22 g) in 60 ml of chloroform and 13.4 ml of chlorosulfonic acid yielded 14.0 g (37 %) of IId as white crystals. A sample recrystallized from 1,2-dichloroethane had m.p. 118−120 °C. (Found: C 36.12; H 4.07; N 6.90; S 15.87. Calc. for $C_6H_7NSO_4.2/3H_2O$: C 35.82; H 4.18; N 6.96; S 15.94). 11.4 g of 2-methoxypyridinium hydrochloride may be isolated from the filtered reaction mixture, bringing the total yield to 76 %.

Ring opening of 3-methoxy pyridinium-1-sulfonate (IId) to give IIId. Disodium, 4-methoxy-5-oxido-trans-*2*,trans-*4-pentadienylidenamin*-N-*sulfonate (IIId)*. 4.0 g of IId was cooled to −20 °C whereupon 2.0 g of sodium hydroxide dissolved in 16 ml of water was added with stirring and cooling. Within 30 min the temperature was raised to 0 °C and 75 ml of 2-propanol was added. The precipitated very unstable yellow crystals were filtered, washed with pentane and dried (20 °C/1 mmHg), to yield 3.5 g (66 %) of IIId. (Found: S 11.28. Calc. for $C_6H_7Na_2NSO_4.2H_2O$: S 11.16).

4-Methyl-5-hydroxy-trans-*2*,trans-*4-pentadienal benzoate (VIb)*. To a suspension of III b (17.3 g) in 104 ml of pyridine was added

benzoyl chloride (8 ml) in 30 min at about −5 °C. Stirring was continued for 1 h and the temperature raised to 20 °C. The resulting yellow suspension was added to 1 litre of ice cold water. Isolation and drying of the precipitated pale yellow crystals yielded 9.12 g (61 %) of Vb, free from any trace of the isomer VIIIb, as seen from the NMR spectra and from TLC. Recrystallization from methanol yielded pale yellow needles m.p. 138−139 °C. (Found: C 72.20; H 5.68. Calc. for $C_{13}H_{12}O_3$: C 72.20; H 5.59).

4-Methyl-5-hydroxy-trans-*2*,trans-*4-pentadienal hexadeuteriobenzoate (VIc)*. The method described above was used. Thus 2.16 g of IIIb yielded 0.55 g (29 %) of VIc as pale yellow needles. A sample recrystallized from methanol had m.p. 137−138 °C. (Found: C 70.17; H+D 5.44. Calc. for $C_{13}H_7D_5O_3$: C 70.55; H+D 5.47).

4-Methoxy-5-hydroxy-trans-*2*,trans-*4-pentadienal benzoate (VId)* was prepared as described above. Thus 2.0 of IIId in 15 ml of pyridine and 1.0 ml of benzoyl chloride was stirred for 15 min at 15 °C, whereupon 300 ml of ice cold water was added, and the precipitated pale yellow needles were isolated yielding 0.46 g (27 %) of VId. Recrystallization from cyclohexane yielded white needles, m.p. 123−124 °C (Found: C 67.30; H 5.19. Calc. for $C_{13}H_{12}O_4$: C 67.23 H 5.21).

4-Methoxy-5-hydroxy-trans-*2*, trans-*4-pentadienal hexadeuteriobenzoate (VIe)* was prepared as above. Thus 2.0 g of IIId and hexadeuteriobenzoyl chloride yielded 0.48 g (27 %) of VIe. Recrystallization from cyclohexane yielded white needles, m.p. 122−123 °C. (Found: C 65.80; H+D 5.12. Calc. for $C_{13}H_7D_5O_4$: C 65.80; H+D 5.06).

2-Bromo-5-hydroxy-trans-*2*,trans-*4-pentadienal benzoate (Xa). Method a*. To IVa (6.0 g) stirred in 150 ml of pyridine at +5 °C was slowly added 2.0 ml of bromine. The clear solution was then cooled to 0 °C and 4.0 ml of benzoyl chloride added; stirring was continued for 5 min, whereupon the reaction mixture was poured into ice cold water (250 ml) and the product isolated. This gave 3.94 g (37 %) of Xa as pale yellow crystals. Recrystallization from methylcyclohexane yielded hygroscopic white needles, m.p. 128−129 °C (d). (Found: C 51.25; H 3.23; Br 28.17. Calc. for $C_{12}H_9BrO_3$: C 51.27; H 3.23; Br 28.43. Ref. 4a gives m.p. 108 °C for this mono brominated derivative.

Method b. To a suspension of 5-hydroxy-*trans*-2,*trans*-4-pentadienal benzoate (VIa) [1] (2.02 g) in 75 ml of ether at +5 °C was added 0.53 ml of bromine and stirring continued for 30 min. Pyridine (35 ml) was then added and after 5 min the reaction mixture was poured into ice cold water (100 ml) and the product was isolated. This gave 2.08 g (72 %) of Xa. Recrystallization from methylcyclohexane yielded analytically pure Xa, mixed m.p. and spectra identical with those of the product from *method a*.

2-bromo-5-hydroxy-trans-*2*-trans-*4-pentadienal hexadeuteriobenzoate (Xb). Method a* described above was used. Thus 2.0 g of I in pyridine (50 ml) was treated with bromine (0.67 ml) at +5 °C, whereupon hexadeuteriobenzoyl chloride (1 ml) was added. Working up as usual yielded 0.74 g (21 %) of Xb as pale yellow crystals. Recrystallization from methylcyclohexane gave colourless needles m.p. 135−136 °C (d). (Found: *J* 50.32; H+D 3.21; Br 27.87. Calc. for $C_{12}H_4D_5BrO_3$: C 50.35; H+D 3.16; Br 27.94.

4-Methyl-trans-*2*,trans-*4-pentadiene-1,5-diol-5-benzoate (VIIb)*. VIIb was prepared by borohydride reduction as described in Ref. 1. Thus VIb (0.50 g) dissolved in 20 ml of dioxane yielded 0.39 g (77 %) of VIIb as colourless unstable needles, m.p. 77−78 °C (benzene-pentane). (Found: C 71.50; H 6.56. calc. for $C_{13}H_{14}O_3$: C 71.54; H 6.47).

2-Bromo-trans-*2*,trans-*4-pentadiene-1,5-diol-5-benzoate (XIa)*. XIa was prepared as above. Thus Xa (0.70 g) in 25 ml of dioxane yielded 0.60 g (86 %) of XIa as white crystals, m.p. 127−128 ° (benzene). (Found: C 50.90; H 3.87; Br 28.00. Calc. for $C_{12}H_{11}BrO_3$: C 50.94; H 3.92; Br 28.22).

2-Bromo-trans-*2*,trans-*4-pentadiene-1,5-diol-5-hexadeuteriobenzoate (XIb)*. XIb was prepared as above. Thus Xb (0.185 g) in 10 ml of dioxane yielded 0.15 g (80 %) of XIb as white crystals, m.p. 138−140 °C (benzene-pentane). (Found: C 49.95; H+D 3.56; Br 27.58. Calc. for $C_{12}H_6D_5BrO_3$: C 50.00; H+D 3.85; Br 27.74).

Reaction of I with methanol−HCl, to give XII and XIII. IVa (25 g) was stirred in 190 ml of methanol and heated to reflux, whereupon 150 ml of methanol containing 0.068 g of HCl was added. Reflux was continued for 10 min and the reaction mixture left overnight at room temperature. Addition of water (600 ml) and potassium carbonate (100 g) to the reaction mixture followed by continuous extraction with ether yielded 12 g of a yellow oil. Distillation of this oil (12 g) gave three fractions: *A*, 3.89 g, b.p. 80−90 °C, n_D^{26} 1.4317; *B*, 4.19 g, b.p. 90−100 °C, n_D^{26} 1.4258; C, 3.48 g, b.p. 100−125 °C, n_D^{25} 1.4232.

Gas chromatography showed fraction *C* to be 95 % pure 1,1,3,5,5-pentamethoxypentane (XIII) corresponding to a yield of 11 % obtained directly by one batch distillation. Analytically pure XIII together with the glutacondialdehyde bis-dimethyl acetal (XII) [6] was obtained by preparative gas chromatography of the crude product. Thus XIII gave n_D^{26} 1.4210. (Found: C 54.00; H 10.02. Calc. for $C_{10}H_{22}O_5$: C 54.03; H 9.95).

Pure 1,1,5,5-tetramethoxy-*trans*-2-pentane (XII) gave n_D^{26} 1.4332. Merländer [6] reported n_D^{20} 1.4288 for XII. (Found: C 56.85; H 9.57. Calc. for $C_9H_{19}O_4$: C 56.82; H 9.54).

2-Methyl-5-hydroxy-trans-*2*,trans-*4-pentadi-*

enal benzoate (VIIIb). The known 2-methyl-1,1,3,5,5-pentamethoxy pentane [5] was hydrolysed to give the crude sodium salt IVb. This salt (0.6 g) in pyridine (6 ml) was treated with 0.5 ml of benzoyl chloride as described in Ref. 1 yielding 0.110 g of cream coloured crystals. Repeated TLC [13] (6 times) with benzene as eluent together with NMR showed these crystals to be a 1:1 mixture of IVb and VIIIb. Recrystallization of a sample from methanol gave colourless crystals m.p. 85 – 90 °C.

In another experiment 1.4 g of the crude product was separated by repeated PTLC to give 0.32 g of VIIIb as colourless needles, m.p. 103 – 105 °C (methanol). (Found: C 71.70; H 5.55). Furthermore this chromatogram yielded 0.35 g of IVb, mixed m.p. and spectra identical with those described for IVb above.

2-Methyl-5-hydroxy-trans-*2*,trans-*4-pentadienal hexadeuteriobenzoate (VIIIc).* VIIIc was prepared as described above. Thus crude IVb (0.8 g) and hexadeuteriobenzoyl chloride (0.6 ml) yielded 0.27 g of a 1:1 mixture of VIIIc and VIc as cream coloured crystals, m.p. 76 – 82 °C. Separation by repeated PTLC of 0.9 g of crude product from another experiment yielded 0.20 g of VIIIc as colourless needles, m.p. 105 – 106 °C (methanol). (Found: C 70.65; H + D 5.57). Furthermore this chromatogram yielded 0.19 g of VIc, mixed m.p. and spectra identical with those previously described for VIc.

Acknowledgements. A sample of 3-methoxypyridine was kindly provided by Dr. N. Clauson-Kaas, Farum, Denmark.

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Received July 15, 1974.