

Preparation and Some Reactions of 1,4-Diaryl-1,3-Butadiene-2,3-Dicarboxaldehyde

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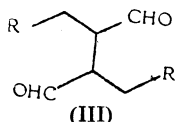
We have succeeded to prepare 1,4-bis-(4-nitrophenyl, 2-chlorophenyl or 1-styryl)-1,3-butadiene-2,3-dicarboxaldehyde (IIIa-c) by condensation of the appropriate aromatic aldehyde with 1,4-butandial (II) in the presence of AcOH/AcOK. Also reduction and oxidation of compounds (IIIa & b) have been studied to give the hydroxy methyl derivatives (IVa & b) and the acid derivatives (Va & b) respectively. Cyclization of the acids (Va & b) yielded the anhydrides (VIa & b).

INTRODUCTION

1,3-butadiene-2,3-dicarboxaldehydes are not only useful in organic synthesis but also they are useful in characterization of amino acids¹. On the other hand, 1,3-butadienes-1,4-diaryl-2,3-dicarboxaldehyde are not well known compounds. This prompted us to throw light upon these compounds by preparing some new ones and studying some of their chemical reaction. El-Gendy *et al.*² succeeded to prepare these unknown compounds by a new method.

RESULTS AND DISCUSSION

The authors extended such important reaction to include the reaction of two moles of aromatic aldehydes, namely, p-nitrobenzaldehyde, o-chlorobenzaldehyde, cinnamaldehyde and/or p-chlorobenzaldehyde with one mole of 1,4-butandial (II) (prepared "in situ" by hydrolysis of 2,5-dimethoxytetrahydrofuran (I) in the presence of acetic acid/potassium acetate mixture) to yield 1,4-bis-[4-nitrophenyl, 2-chlorophenyl, 1-styryl or 4-chlorophenyl]-1,3-butadiene-2,3-dicarboxaldehyde (IIIa-d) respectively.



a, R = C₆H₄.NO₂-p; b, R = C₆H₄.Cl-o; c, R = C₆H₄.CH=CH-;
d, R = C₆H₄.Cl-p

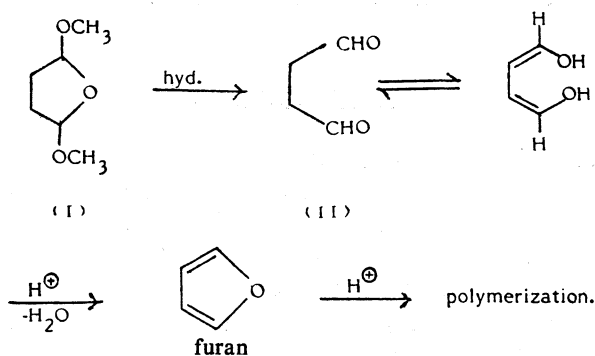
The assigned structure for compounds (IIIa-d) was established by

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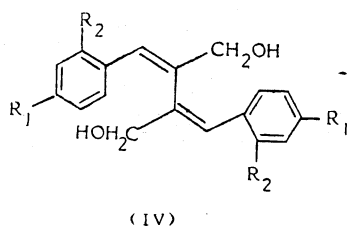
(i) IR spectra showing bands at 2840, 2920, 2745, 2715 characteristic of

$\nu-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$ of dialdehydes and in the region (1680–1655) due to $\nu(\text{C}=\text{O})$, (ii) UV(CHCl_3)³ of compounds (IIIa-d) showed λ_{max} 330 log $\epsilon(4.7)$, λ_{max} 280(4.6) and λ_{max} 345(4.45) respectively, (iii) ^1H NMR of compounds (IIIa-d) showed signals at 7.35 (s, 8H, aromatic protons); 7.60 (s, 2H, $-\text{C}=\text{CH}$); 9.6 (s, 2H, CHO) of (IIIa); at 7.4 (s, 8H, aromatic protons); 7.65 (s, 2H, $-\text{C}=\text{CH}$) and at 9.75 (s, 2H, $-\text{CHO}$) of (IIIb) and at 7.4 (m, 10H, aromatic protons), 7.75 (m, 6H, olefinic protons) and at 9.8 (s, 2H, $-\text{CHO}$) of (IIIc) which confirm the proposed structure.

The poor yield of these compounds (IIIa-c) may be interpreted by the fact that the end form of the butandial (II) can be dehydrated to give furan which polymerises in acid medium as follows:



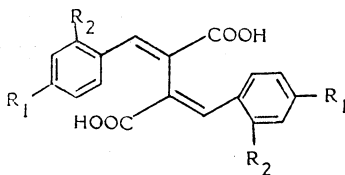
As a point of interest, the compounds (IIIb) and/or (IIIc) were reduced by potassium borohydride to afford 2,3-bis-(hydroxymethyl)-1,4-bis-(2-chlorophenyl or 4-chlorophenyl)-1,3-butadiene (IVa & b) respectively.



a, $\text{R}_1 = \text{H}$; $\text{R}_2 = \text{Cl}$, *b*, $\text{R}_1 = \text{Cl}$; $\text{R}_2 = \text{H}$

The structure of compounds (IVa & b) was confirmed by: (i) IR spectra which showed band in the region (3320–3330) due to νOH and absence of any band in the region (1690–1650) $\nu\text{C}=\text{O}$, (ii) UV(CHCl_3) showed λ_{max} at 256 nm for (IVa), λ_{max} at 258 nm for (IVb).

On the other hand, compounds (IIIb) & (IIIc) when allowed to oxidise with silver oxide in boiling ethanol yielded 1,4-bis-(2-chlorophenyl or 4-chlorophenyl)-1,3-butadiene-2,3-dicarboxylic acids (Va & b) respectively.

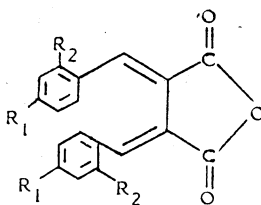


(v)

a, $R_1 = H$; $R_2 = Cl$; *b*, $R_1 = Cl$; $R_2 = H$

The structure of compounds (Va & b) was confirmed by: (i) IR spectra which showed bands at 3200 and 1690 due to νOH & $\nu C=O$ (acid) respectively, (ii) UV (dioxan) showed λ_{max} at 300 nm and at 304 nm for (Va & b) respectively.

Treatment of compounds (Va & b) with acetyl chloride yielded bis-(2-chlorobenzylidene or 4-chlorobenzylidene) succinic anhydride (VIa & b) respectively.



(vi)

a, $R_1 = H$; $R_2 = Cl$; *b*, $R_1 = Cl$; $R_2 = H$

The structure of compounds (VIa & b) was supported by IR spectra which showed absorption bands at 1820 and at 1760 due to $\nu C=O$ (anhydride).

EXPERIMENTAL

All melting points reported are uncorrected and were measured by the open capillary method, microanalyses were carried out in the micro-analytical center, Cairo University, Egypt. The IR spectra (KBr) were recorded on Beckmann Acculab-6, and PYE Uni-a cam Sp. (max. in cm^{-1}). UV spectra were recorded on Varian Super Scan-3 Spectrophotometer and H^1NMR spectra in $CDCl_3$ were run on EM-360,60 MHz NMR spectrometer using TMS as the internal reference (chemical shifts in δ scale).

Synthesis of 1, 4-Bis-(4-Nitrophenyl or 2-Chlorophenyl or 1-Styryl)-1, 3-Butadiene-2, 3-Dicarboxaldehyde (III a-d)

A mixture of 2, 5-dimethoxytetrahydrofuran (0.01 mole), aromatic aldehydes (0.02 mole) namely, p-nitrobenzaldehyde, o-chlorobenzaldehyde, cinnamaldehyde and/or p-chlorobenzaldehyde, acetic acid (1 ml), water (1 ml), and potassium acetate (2 g) was heated under reflux for 5 hrs. After cooling, the mixture was poured into water (20 ml), then steam distilled for elimination of the unreacted aldehydes.

The mixture was then extracted with ethyl acetate. The extract was washed with NaHCO₃ and water, then treated with animal charcoal, filtered, and concentrated. The separated crystals were filtered off and crystallized from the suitable solvent (cf. Table 1).

TABLE 1

Product	M.P. °C.	Yield %	Solvent	Molecular formula (M. wt.)	Analysis	
					Calcd.	Found
IIIa	90	40	Ethanol	C ₁₈ H ₁₁ O ₆ N ₂ (352)	C 61.36 H 7.95 N 3.41	61.27 7.93 3.39
IIIb	165	45	Ethanol	C ₁₈ H ₁₂ O ₂ Cl ₂ (331)	C 65.26 H 3.63	65.30 3.71
IIIc	85	40	Benzene	C ₂₂ H ₁₈ O ₂ (314)	C 84.08 H 5.73	84.10 5.69
IIId	120	60	Ethanol	C ₁₈ H ₁₂ O ₂ Cl ₂ (331)	C 65.26 H 3.63	65.30 3.71
IVa	90	50	Benzene	C ₁₈ H ₁₆ O ₂ Cl ₂ (335)	C 64.48 H 4.78	64.39 4.75
IVb	113	82	Benzene	C ₁₈ H ₁₆ O ₂ Cl ₂ (335)	C 64.48 H 4.78	64.47 4.76
Va	120	80	—	C ₁₈ H ₁₂ O ₄ Cl ₂ (363)	C 59.50 H 3.31	59.42 3.29
Vb	145	75	—	C ₁₈ H ₁₂ O ₄ Cl ₂ (363)	C 59.50 H 3.31	59.48 3.32
VIa	156	50	—	C ₁₈ H ₁₀ O ₃ Cl ₂ (345)	C 62.61 H 2.90	62.53 2.91
VIb	184	52	—	C ₁₈ H ₁₀ O ₃ Cl ₂ (345)	C 62.61 H 2.90	62.58 2.80

Formation of 2, 3-Bis-(Hydroxymethyl)-1, 4-Bis-(2-Chlorophenyl or 4-Chlorophenyl)-1, 3-Butadiene (IVa & b)

1, 4-Bis-(2-chlorophenyl)-butadiene-2, 3-dicarboxaldehyde (IIIb) and/

or 1, 4-bis-(4-chlorophenyl)-butadiene-2,3-dicarboxaldehyde (IIIId)(0.02 mole) and methanol (30 ml) were added to potassium borohydride (0.04 mole). The mixture was stirred for 5 hrs, poured into ice/water (400 g) and extracted with ether to give after concentration colourless crystals of (IVa & b) (cf. Table 1).

Formation of 1, 4-Bis-(2-Chlorophenyl or 4-Chlorophenyl)-1, 3-Butadiene-2, 3-Dicarboxylic acid (Va & b)

A mixture of dialdehyde (IIIb) and/or (IIIId) (0.01 mole), silver nitrate (0.04 mole) and 50% ethanol (6 ml) was boiled during 4 hrs, then diluted with water (10 ml) and filtered. The filtrate was acidified with N-HCl (10 ml) and extracted with ether.

The organic layer was washed with water and dried with sodium sulphate. After solvent elimination the diacids were obtained (Va & b) (cf. Table 1).

Formation of Bis-(2-Chlorobenzylidene or 4-Chlorobenzylidene)-succinic anhydride (VIa & b)

The diacid (VI) and/or (Vb) (0.01 mole) was dissolved in acetyl chloride (6 ml). After allowing the mixture to stand overnight, the acetyl chloride was evaporated and the resultant oil washed with a small amount of ether to give (VIa & b) (cf. Table 1).

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