SYMMETRICAL AND UNSYMMETRICAL DERIVATIVES OF DISTYRYLBENZENE

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The symmetrically substituted derivatives *I—V* of 1,4-distyrylbenzene have been prepared *via* the Horner reaction. A modification of the latter enabled preparation of unsymmetrical derivatives of 1,4-distyrylbenzene.

Symmetrical derivatives of 1,4-distyrylbenzene belong to disperse optical brightening agents applied especially to polyester fibers. In addition the compounds of this type are used as potentiators in sensibilization of photographic emulsions. No method of preparation of unsymmetrical derivatives of distyrylbenzene has been found yet. The symmetrical derivatives of 1,4-distyrylbenzene are prepared by reaction of benzyltriphenylphosphonium halogenides or dialkyl benzylphosphonates with aromatic aldehydes[1-7]. The necessary phosphonates are obtained by reaction of benzyl chloride derivatives with triethyl, diisobutyl or dimethyl phosphite. In practical application triethyl phosphite is used almost exclusively now[8-10], although its reaction course and yields are less advantageous than those of diisobutyl phosphite[11,12]. The reaction with triethyl phosphite is simple, whereas diisobutyl and dimethyl phosphites must be transformed into sodium salt by sodium ethoxide before the proper condensation with the corresponding benzyl chloride[13]. The same method can be used for preparation of a bifunctional phosphite *e.g.* from 1,4-bis(chloromethyl)benzene. The condensation of phosphonium salt or phosphonate with aromatic dialdehyde or, on the contrary, that of a bifunctional phosphonium salt with a monoaldehyde has a simple course and high yields in high-boiling solvent (usualy N,N-dimethylformamide) in the presence of methanolic potassium hydroxide or sodium alkoxide. The non-symmetrical derivatives of 1,4-distyrylbenzene cannot be prepared in this way.

In our work the Horner reaction was used for synthesis of the distyrylbenzene derivatives *I—V*.* Condensation of the diphosphorane *XIV* with benzaldehyde

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* The compounds *I* and *III* were prepared before from benzyl- and 4-chlorobenzyltriphenylphosphonium chloride, respectively, by action of ethyllithium.[14]

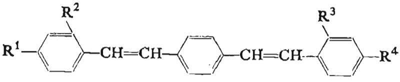
gave 1,4-distyrylbenzene, that with 4-chlorobenzaldehyde gave 1,4-bis(4-chlorostyryl)benzene (*III*), and that with 2-chlorobenzaldehyde gave 1,4-bis(2-chlorostyryl)benzene (*IV*). 1,4-Bis(2-methylstyryl)benzene (*II*) was prepared by reaction of dimethyl-(2-methylbenzyl)phosphonate (*XII*) with terephthalic dialdehyde. The condensations were carried out in dimethylformamide by action of methanolic KOH.

Course of the condensation reaction of phosphonates with terephthalic dialdehyde depends on the reaction medium and on substituents in the aromatic part of the phosphonate. Whereas in dimethylformamide or xylene the reaction is very fast and gives a practically uniform derivative of distyrylbenzene, in aqueous medium the reaction course is very slow giving the styrylbenzaldehyde derivative. The dependence of the reaction on substituents in benzyl group of the phosphonate is seen *e.g.* in that dimethyl 2-cyanobenzylphosphonate (*XIII*) reacts easily with terephthalic dialdehyde to give 4-(2-cyanostyryl)benzaldehyde (*VI*), whereas methyl- (*XII*), chloro- (*XI*) or methoxycarbonylderivative (*XV*) of the phosphonate do not react under the same conditions. 4-(2-Cyanostyryl)benzaldehyde (*VI*) is formed in 50% yield by reaction of dimethyl 2-cyanobenzylphosphonate (*XIII*) with terephthalic dialdehyde in water in the presence of sodium hydroxide. The cyanostyrylbenzaldehyde *VI* can react further with another molecule of dimethyl benzylphosphonate derivative to give unsymmetrical derivatives of distyrylbenzene. In this way we prepared 1-(2-methylstyryl)-4-(2-cyanostyryl)benzene (*VII*), 1-(3-chlorostyryl(-4-(2-cyanostyryl)benzene (*VIII*) and 1-(2-cyanostyryl)-4-(4-methoxycarbonylstyryl)benzene (*IX*). 4-(2-Cyanostyryl)benzaldehyde reacts easily with the diphosphonate compound *XIV* to give the polyene *V*, and it also undergoes the Knoevenagel reaction with 2,5,6-trimethylbenzoxazole to give 5,6-dimethyl-2-(4-(2-cyanostyryl)styryl)benzoxazole[14] (*X*). All the prepared substances *I*–*X* show strong fluorescence and good solubility in usual organic solvents except for the compound *V* which is only soluble in dimethylformamide or pyridine. The compounds can be separated chromatographically on silica gel using benzene as eluent. The necessary condensation intermediates dimethyl 4-chlorobenzyl-(*XI*), 2-chlorobenzyl-(*XII*) and 2-cyanobenzylphosphonates (*XIII*) were prepared by reaction of sodium dimethyl phosphite with the respective benzyl chlorides in benzene. The phosphonates were not purified and were used for further reactions in excess. The diphosphonate compound *XIV* was prepared according to refs[15,16] by condensation of excess triethyl phosphite with 1,4-bis(chloromethyl)benzene.

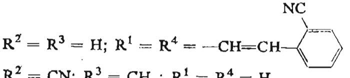
EXPERIMENTAL

1,4-Xylylene-bis(diethyl phosphonate) (*XIV*)

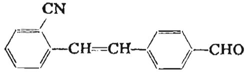
Solution of 17·5 g 1,4-bis(chloromethyl)benzene and 68·6 ml (66·4 g) triethyl phosphite was heated at 150°C 10 h. After distillation of excess triethyl phosphite (31 ml) and cooling, 36 g solid diphosphonate was obtained which was used immediately in the subsequent reaction.

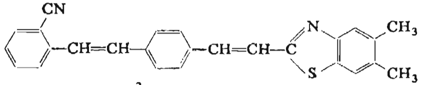


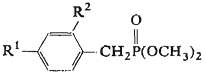
I, $R^1 = R^2 = R^3 = R^4 = H$
II, $R^2 = R^3 = CH_3$; $R^1 = R^4 = H$
III, $R^2 = R^3 = H$; $R^1 = R^4 = Cl$
IV, $R^2 = R^3 = Cl$; $R^1 = R^3 = H$

V,


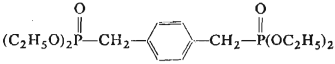
VII, $R^2 = CN$; $R^3 = CH_3$; $R^1 = R^4 = H$
VIII, $R^2 = CN$; $R^4 = Cl$; $R^1 = R^3 = H$
IX, $R^2 = CN$; $R^4 = COOCH_3$; $R^1 = R^3 = H$

VI,


X,




XI, $R^2 = H$; $R^1 = Cl$
XII, $R^2 = CH_3$; $R^1 = H$
XIII, $R^2 = CN$; $R^1 = H$
XV, $R^2 = H$; $R^1 = COOCH_3$

XIV,


Dimethyl Benzylphosphonate Derivatives *XI*—*XIII*, *XV*

Suspension of 76 g (0·5 mol) 2-cyanobenzyl chloride, 60 g (50 ml) dimethyl phosphite and 200 ml benzene was heated until dissolution, cooled and treated with methoxide solution (13 g sodium in 200 ml methanol) added dropwise below 40°C within 45 min. After the addition of sodium methoxide the solution was boiled 30 min, 300 ml solvent was distilled off, and the precipitated salt was dissolved by addition of 300 ml water. The oily phosphonate layer was separated, and the aqueous layer was extracted with benzene. The benzene extracts were combined with the main portion, the solution was dried with anhydrous sodium sulphate, and benzene was distilled off. The residue was treated with 12·5 ml ethanol, the solution was cooled on an ice bath, and the precipitated dimethyl 2-cyanobenzylphosphonate (*XIII*) was collected by suction and washed with ether. On several hours standing the filtrate gave further precipitate of the phosphonate. Yield 13·97 g (58%) raw product, m.p. 73—74°C. Similar procedure was applied for preparation of dimethyl 4-methoxycarbonylbenzylphosphonate (*XV*), b.p. 184°C/0·533 kPa (yield 50%), dimethyl 2-chlorobenzylphosphonate (*XI*) and dimethyl 2-methylbenzylphosphonate (*XII*); the latter two compounds had vaseline consistency and were used immediately in subsequent reaction steps.

1,4-Bis(2-methylstyryl)benzene (*II*)

Solution of 1·68 g KOH in 20 ml ethanol was added drop by drop to solution of 4 g (0·022 mol) dimethyl 2-methylbenzylphosphonate (*XII*) and 1·34 g (0·01 mol) terephthalic dialdehyde in 18 ml dimethylformamide at 20°C during 15 min, whereupon a yellow solid precipitated. The temperature increased spontaneously to 40°C. After further heating at 60°C 30 min, cooling at 20°C,

TABLE I

Yields, Melting Points, and Elemental Analyses of Distyrylbenzene Derivatives

Compound	Yield, % m.p., °C	Formula (m.mass)	Calculated/Found			
			% C	% H	% N	% Cl
I	55	$C_{22}H_{14}$	93·57	6·43	—	—
	259—260[a]	(282·3)	93·23	6·51	—	—
II	35	$C_{24}H_{18}$	92·86	7·14	—	—
	178—179[b]	(310·4)	92·91	7·24	—	—
III	25	$C_{22}H_{12}Cl_2$	75·24	4·59	—	20·17
	286 decomp.[a]	(351·3)	74·73	4·67	—	19·96
IV	25	$C_{22}H_{12}Cl_2$	75·24	4·59	—	20·17
	166—167[b]	(351·3)	75·58	4·24	—	20·31
V	6·5	$C_{40}H_{24}N_2$	—	—	5·22	—
	310—312[c]	(536·6)	—	—	5·41	—
VI	43	$C_{16}H_{10}NO$	82·38	4·75	6·01	—
	150—151[d]	(233·3)	82·19	4·41	6·38	—
VII	9	$C_{24}H_{15}N$	89·68	5·96	4·36	—
	158—159[b]	(321·4)	89·30	5·88	4·46	—
VIII	48	$C_{23}H_{12}ClN$	80·81	4·72	4·10	10·37
	185—186[b]	(341·9)	80·90	5·14	4·18	10·38
IX	90	$C_{25}H_{15}NO_2$	82·17	5·24	3·83	—
	206—207[b]	(365·4)	81·68	5·34	3·87	—
X	81·5	$C_{26}H_{20}N_2O$	82·95	5·36	7·44	—
	256—266[a]	(376·4)	82·84	5·50	7·48	—

[a] Chlorobenzene; [b] benzene; [c] dimethylformamide; [d] ethanol.

and addition of 40 ml water the precipitate was collected by suction and washed with 10 ml 50% ethanol and 10 ml water. Yield 1·09 g (35%) 1,4-bis(2-methylstyryl)benzene (*II*), m.p. 178--179°C (benzene). The elemental analysis is given in Table I.

Symmetrical Distyrylbenzene Derivatives *I*, *III*, *IV*

Sodium ethoxide solution (0·8 g Na in 20 ml ethanol) was added dropwise to solution of 0·01 mol 1,4-xylylene-bis(diethyl phosphonate) (*XIV*) and 0·02 mol benzaldehyde derivative in 20 ml dimethylformamide at 30°C. The suspension was treated with 10 ml ethanol and heated at 60°C 30 min. The separated product was collected by suction at 20°C and washed with 20 ml ethanol and 100 ml hot water. The yields, melting points and elemental analyses are given in Table I.

Polyene *V*

Solution of 1·7 g KOH in 20 ml methanol was added to solution of 1·9 g diphosphonate *XIV*, 2·33 g 4-(2-cyanostyryl)benzaldehyde (*VI*), 30 ml dimethylformamide and 20 ml methanol. On boiling the solution separated a yellow fluorescent solid which was, the other day, collected by suction and washed with methanol. Yield 0·35 g, m.p. 210—213°C. The elemental analysis is given in Table I.

4-(2-Cyanostyryl)benzaldehyde (*VI*)

3·60 g Dimethyl 2-cyanobenzylphosphonate (*XIII*), 2·72 g terephthalic dialdehyde and 200 ml water heated until dissolution and alkalized with 2·5M-NaOH to weak alkaline reaction. After five minutes boiling the separated solid was collected by suction while hot and washed twice with hot water. Yield 1·6 g (43%) 4-(2-cyanostyryl)phosphonate (*VI*), m.p. 150—151°C (ethanol). The elemental analysis is given in Table I.

Unsymmetrical Distyrylbenzene Derivatives *VII*—*IX*

Solution of 1·7 g KOH in 20 ml ethanol was added to solution of 0·01 mol 4-(2-cyanostyrylbenzaldehyde and 0·02 mol dimethyl benzylphosphonate derivative (100% excess) in 20 ml dimethylformamide. After 30 min heating at 60°C the precipitated solid was collected by suction and washed with little ethanol. The yields, melting points and elemental analyses are given in Table I.

5,6-Dimethyl-2-(4-(2-cyanostyryl)styryl)benzoxazole (*X*)

A mixture of 3·8 g 3,4-dimethyl-6-N-acetamidophenol and 4·66 g 4-(2-cyanostyryl)benzaldehyde (*VI*) was added to solution of 2 g 4-dodecylbenzenesulphonic acid, 8 ml 1,2-dichlorobenzene and 0·8 ml aqueous ammonia (25%). The mixture was slowly heated up to 186°C with simultaneous removal of water by distillation. After the reaction was finished, 4·8 ml 1,2-dichlorobenzene was distilled off, the residue was cooled and diluted with 10 ml ethanol, and the separated solid was collected by suction and washed with 15 ml acetone. Yield 6·13 (81·5%) yellow fluorescent solid, m.p. 263—265°C (chlorobenzene-benzene). The elemental analysis is given in Table I.

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