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Reaction of Aromatic *p*-Substituted Bisphosphoranes with Bisaldehydes[1]

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The Wittig reaction of aromatic *p*-substituted bisphosphoranes with bisaldehydes was carried out in dimethylformamide to give four kinds of poly-*p*-xylylidene series, as the oligopolymers in good yield. In the process of the reaction, the cyclic olefins were also given in very poor yield.

In recent papers[3] several attempts on synthesis of ring type of olefinic compounds by means of the Wittig reaction have been reported. Especially, Sondheimer and his co-workers[4] succeeded to prepare some interesting olefinic ring compounds in this field. On the contrary there are a few reports[5] on the synthetic studies of linear oligopolymers.

Approaching and synthetic possibility to obtain some desired linear oligopolymers by the Wittig reaction suggests that two modes of synthesis are conceivable, that is, one mode is that one side of a monomer is substituted by one phosphorane group and opposite side substituted by one carbonyl group. Another is a pair of one monomer disubstituted by carbonyl group with one more disubstituted by phosphorane group at the both sides of each monomer. In the latter type, the synthesis of poly-*p*-xylylidene (XIIIa) as an oligopolymer (Chart 2) has only been reported by McDonald and his co-worker.[5a] As this procedure seemed to be convenient for this first object of our work, we attempted to prepare some linear oligopolymers according to McDonald's method,[5a] although in the formation of olefinic compounds the

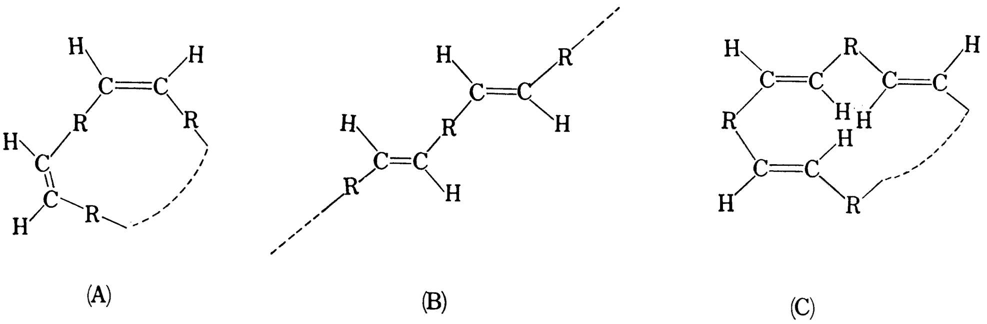

Fig. 1. Mode of Polymerization by the Wittig Reaction

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[1] Presented at the 90th Annual Meeting of the Pharmaceutical Society of Japan at Sapporo, July 1970.

[2] Location: *Katakasu, Fukuoka.*

[3] C.E. Griffin, K.R. Martin and B.E. Douglas, *J. Org. Chem.*, **27**, 1627 (1962); R. Breslow, W. Horspool, H. Sugiyama and W. Vitale, *J. Am. Chem. Soc.*, **88**, 3677 (1967); K. Dirmoth, G. Pohl and H. Follmann, *Chem. Ber.*, **99**, 634 (1966).

[4] K. Grohmann and F. Sondheimer, *J. Am. Chem. Soc.*, **89**, 7119 (1967); J.A. Elix and M.V. Sargent, *ibid.*, **89**, 5080 (1967); J.A. Elix and M.V. Sargent, *ibid.*, **90**, 1631 (1968); J.A. Elix, F. Sondheimer and M.V. Sargent, *ibid.*, **92**, 973 (1970).

[5] *a*) R.N. McDonald and T.W. Campbell, *J. Am. Chem. Soc.*, **82**, 4669 (1960); *b*) A. Maercker, "Organic Reactions," Vol. 14, ed. by John Wiley and Sons, Inc., New York, 1965, p. 329 (A. Haag, Doctoral Dissertation, Universität Heidelberg, 1962); *c*) E.E. Schweizer, C.J. Berniger, D.M. Crouse, R.A. Devis and R.S. Logothetis, *J. Org. Chem.*, **34**, 207 (1969).

cis-trans isomerization of the Wittig reaction is usually detectable. Because of that in general *cis* bonds in such molecules are not preferable to form linear molecular skeleton, the olefinic precursors involving some *cis* bonds tend to form some olefinic ring compounds according as conditions of the reaction (Fig. 1a). Originally nonlinear monomers, even if in *trans* olefination, may have in any case possibility to lead to comparatively large olefinic ring compounds with increasing of polymerization degree (Fig. 1c). Consequently in order to keep away from such olefinic cyclization as much as possible, a pair of *p*-bisphosphoranes with *p*-biscarbonyl components was especially used as reactant for this work. In practice the Wittig reaction of phosphonium salts with carbonyl components was carried out in dimethyformamide with lithium ethoxide as ylid forming reagent.

For example *p*-xylylene-bis(triphenylphosphonium chloride) (Ia)[6] and 2,5-dimethoxy-*p*-xylylene-bis(triphenylphosphonium chloride) (Ib) as ylid component, and further terephthalaldehyde (VIIIa), 2-nitroterephthalaldehyde (VIIIb)[7] and 9,10-anthracenedicarboxaldehyde (XVII)[8] as bicarbonyl component were used, respectively. Generally, the olefinic oligopolymers obtained were mostly the *cis* and *trans* isomeric mixtures. Therefore it was too difficult to isolate the each desired pure geometrical isomer only from the each corresponding reaction mixture due to less solubility in the usual organic solvents and more complicated formation of *cis, trans* isomers in the reaction system.

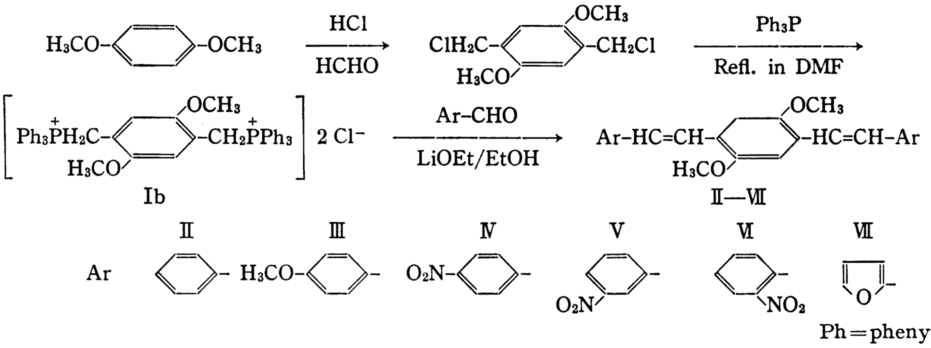

Chart 1

Bisphosphonium salt (Ib) was prepared by the reaction of triphenylphosphine with 2,5-bis(chloromethyl)hydroquinone dimethylether[9] in dimethylformamide prepared from hydroquinone dimethylether by chloromethylation (Chart 1). Bisphosphonium salt (Ib) and six aldehydes were respectively submitted to the Wittig reaction for the purpose of examining reactivity to the each aldehyde group (Chart 1). The operation resulted in the formation of the corresponding distyrylbenzene derivatives (II—VI) and 1,4-bis[2-(2-furyl)vinyl]-2,5-dimethoxybenzene (VII) in good yield, respectively (Table I). These data implied that the bisphosphonium salt (Ib) is very active to the Wittig reaction. In order to purify the crude olefinic products obtained, silicagel column chromatography or fractional recrystallization was undertaken with appropriate solvents, however, except compound (IV), we could not isolate by any means each anticipated *cis, trans* stereoisomer in pure state, because the stereoisomeric mixtures having one or two *cis* bonds in those molecules are very changeable in the process of purification. Therefore, other compounds (II, III, V, VI, and VII) were perspectively recrystallized from some favorable solvents (benzene, cyclohexane and xylene) in the presence of catalytic amount of iodine[6] (Table I). However, the compound (IV) was suc-

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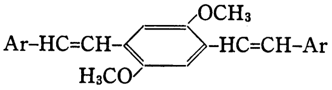
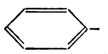
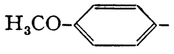
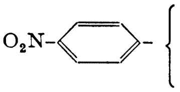
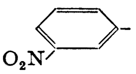
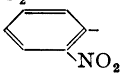
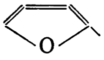
6) T.W. Campbell and R.N. McDonald, *J. Org. Chem.*, **24**, 1246 (1959).
7) P. Ruggli and E. Preiswerk, *Helv. Chim. Acta*, **22**, 484 (1939).
8) B.H. Klanderman, *J. Org. Chem.*, **31**, 2619 (1966).
9) J.H. Wood and R.E. Gibson, *J. Am. Chem. Soc.*, **71**, 393 (1949).

Table I. Appearance and Analytical Data of 

$Ar-HC=CH-C_6H_2(OCH_3)_2-HC=CH-Ar$

No.	Ar	Appearance (recryst. solv.)	mp (°C)	Yield[a] (%)	IR KBr (cm^{-1}) -HC=CH-	$\lambda_{max}^{1,2-C_2H_4Cl_2}$
II		green-yellow needles (benzene)	190—190.5	75	960	325 390
III		green-yellow prisms (benzene)	219—221	97	967	332 394
IVa		yellow needles (DMSO)	230	88 (total)	—	408
IVb		red needles (DMSO)	301		967 955	358 440
V		orange prisms (xylene)	273—275	95	960	328 410
VI		red needles (benzene)	249.5—250	90	960	323 410
VII		yellow prisms (cyclohexane)	188	93	968	346 401

No.	$\varepsilon\times10^{-4}$	*Anal.* (%) Calcd. Found C	H	N	NMR σ (ppm)[b] (in DMSO-d_6) Olefinic proton	J (cps)	OCH_3	Configuration
II	2.58 3.38	84.17 84.20	6.49 6.22	— —	7.54 (d) 7.08 (d)	16.5 16.5	3.91	trans, trans
III	2.25 4.74	77.59 77.67	6.51 6.36	— —	7.16 (s) 7.13 (s)	—	3.84 3.92	trans, trans
IVa	3.04	66.66 66.59	4.66 4.74	6.48 6.38	6.82 (s)	—	3.43	cis, cis
IVb	2.02 4.45	66.66 66.68	4.66 4.60	6.48 6.85	7.58 (s) 7.53 (s)	—	3.97	trans, trans
V	2.89 3.31	66.66 66.53	4.66 4.62	6.48 6.00	7.53 (s)	—	3.96	trans, trans
VI	2.47 2.40	66.66 66.93	4.66 4.61	6.48 6.04	7.70 (d) 7.35 (d)	16.5 16.5	3.92	trans, trans
VII	2.10 4.22	74.52 74.34	5.63 5.35	— —	6.92 (d) 7.36 (d)	16.5 16.5	3.88	trans, trans

a) calcd. on the basis of phosphonium salt
b) s: singlet, d: doublet

cessfully separated two crystal forms from a mixture of benzene and chloroform. Furthermore each recrystallization of the two crystal forms from dimethylsulfoxide led to the two pure crystal forms, one is yellow needles, mp 230° (IVa) and another is red needles, mp 301° (IVb).

Infrared (IR) spectra (in KBr) of every compound (II, III, IVb, V, VI, and VII) fell in the range of 955 to 968 cm^{-1} assignable to *trans*-1,2-disubstituted olefin.[10] The compound (IVa) was deduced to be *cis, cis* configurafion from the evidence of the absence of IR absorption band attributable to *trans*-1,2-disubstituted olefin and from making easy to convert it to *trans,*

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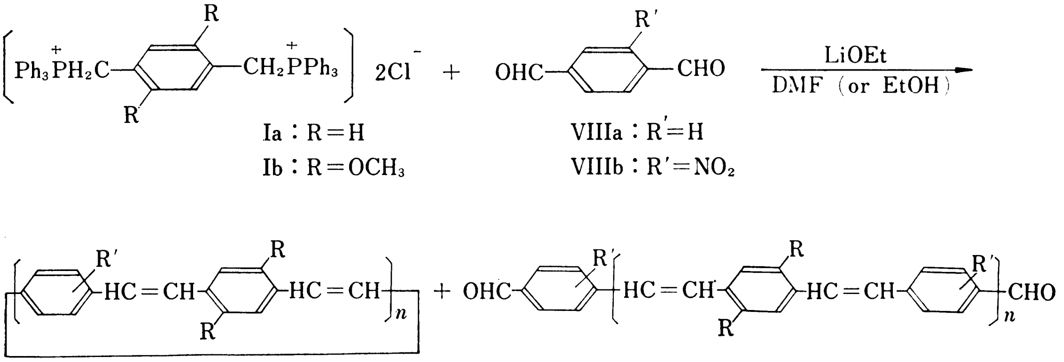
[10] L.J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed by John. Wiley and Sons, Inc., New York, 1958, pp. 34, 45—49.

trans configuration even in the course of recrystallization from the appropriate solvents (benzene or xylene) containing catalytic amount of iodine. Additionally, on the basis of each result of nuclear magnetic resonance (NMR) spectral observation (in dimethylsulfoxide-d_6) of the compounds (II, III, IVa, V, VI and VII), a possibility of asymmetrical *cis, trans* configuration was negative because of singlet signal attributable to methoxy proton (Table I).

Especially, the results of NMR spectra of the compounds (II, VI and VII) exhibit two-doublets attributable to olefinic proton and also coupling constant, 16.5 cps[11) of *trans*-1,2-disubstituted olefin (Table I). Accordingly the above facts support that the compounds (II, VI and VII) are in *trans, trans* configuration. The others (III, IVa, IVb, and V) each seem to be in singlet or doublet and absent of corresponding coupling constant, *ca.* 16.5 cps, respectively. In comparing with the NMR spectra (in dimethylsulfoxide-d_6) between IVa and IVb, the absorption band attributable to olefinic proton of the latter at the lower magnetic field than that of IVa supports that the configuration of (IVa) must be *cis,cis* and (IVb) *trans, trans*,[12) and besides the *trans,trans* configuration of both compounds of III and V was confirmed in comparing with the NMR spectral data of the other compounds (II, IVb, VI and VII) (Table I).



Ia : R=H
Ib : R=OCH$_3$

VIIIa : R′=H
VIIIb : R′=NO$_2$

IX : R=H, R′=H, n=2, 3
X : R=OCH$_3$, R′=H, n=2
XIa : R=H, R′=NO$_2$, n=2
XIb : R=H, R′=NO$_2$, n=3
XII : R=OCH$_3$, R′=NO$_2$, n=2

XIIIa : R=H, R′=H, $\bar{n}$=4.5[a)
XIIIb : R=H, R′=H, $\bar{n}$=5(in EtOH)
XIIIc : R=H, R′=H, $\bar{n}$=7
XIV : R=OCH$_3$, R′=H, $\bar{n}$=7
XV : R=H, R′=NO$_2$, $\bar{n}$=11
XVI : R=OCH$_3$, R′=NO$_2$, $\bar{n}$=5

Ph=phenyl

a) R. N. McDonald and J. W. Campbell, *J. Am. Chem. Soc.*, **82**, 4669 (1960)

Chart 2

Getting in the main subject, we carried the Wittig reaction of bisaldehyde (VIIIa) with bisphosphonium salt (Ia) in ethanol to obtain poly-*p*-xylylidene (XIIIb : n=5) in almost quantitative yield and a trace of yellowish crystalline powder (Chart 2). The powdery substance seemed to be a mixture of some cyclic olefins and lower molecular weight linear oligopolymers (n<5) on the basis of a molecular ion peak analysis[13) in the mass spectra. McDonald has announced the synthesis of poly-*p*-xylylidene (XIIIa : n=4.5) from bis-

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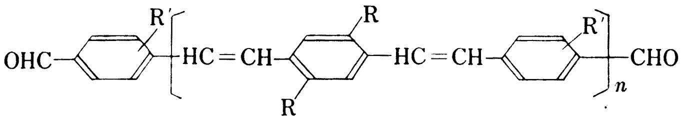
11) R.M. Silverstein and G.C. Bassler, "Spectrometric Identification of Organic Compounds," 2nd ed. by John Wiley and Sons, Inc., New York, 1967, p. 144 (compiled by Varian Associates).
12) L.M. Jackmann and R.H. Wiley, *Proc. Chem. Soc.*, **1958**, 196.
13) R.M. Silverstein and G.C. Bassler, "Spectrometric Identification of Organic Compounds," 2nd ed. by John Wiley and Sons, Inc., New York, 1967, pp. 9—11.

phosphonium salt (Ia) with bisaldehyde (VIIIa).[5a)] We attempted, however, to obtain more higher polymerization products using dimethylformamide as reaction solvent in the reaction. As may be seen from Table II, it was proved that dimethylformamide was more effective to promote the polymerization as much as possible, and the solvent resulted in the formation of a little higher polymerized oligopolymer (XIIIc : $n=7$) than ethanol (Table II). And also in the three pairs of Ia-VIIIb, Ib-VIIIa and Ib-VIIIb, the corresponding poly-*p*-xylylidenes (XIV, XV, and XVI) were prepared in good yield, respectively. The average degree of polymerization ($\bar{n}$) of such the new oligopolymers obtained could approximately be deduced from the elementary analytical data (Table II). Additionally bromination of the above oligopolymers was readily carried out in carbon tetrachloride to yield the each corresponding bromide as colorless or pale yellow crystalline powder. On the basis of the disappearance of the characteristic olefinic double bond absorption (*ca.* 960 cm^{-1}, or so) of IR spectra (in KBr) on the each bromide and the agreement of the elementary analytical data, the average values of polymerization degree were fairly supported (Table II).

Detection of the IR spectra (in KBr) attributable to carboxaldehyde group (*ca.* 1690 cm^{-1}) at the both ends of the oligopolymer instead of triphenylphosphonium group (1100—1120 cm^{-1}),[14)] suggests the existence of carboxaldehyde groups as end group in the oligopolymers.

TABLE II. Poly-*p*-xylylidene Series



No.	R	R'	Appearance	mp (°C)	IR KBr (cm^{-1}) $\nu_{C=O}$	IR KBr (cm^{-1}) H>C=C<H
XIIIb	H	H	lemon yellow cryst. powder	>340	1690	960
XIIIc	H	H	lemon yellow cryst. powder	>340	1695	957
XIV	OCH_3	H	orange yellow cryst. powder	*ca.* 170	1690	962
XV	H	NO_2	orange cryst. powder	*ca.* 200	1690	960
XVI	OCH_3	NO_2	reddish orange cryst. powder	*ca.* 230	1700	962

No.	*Anal.* (%) Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N	*Anal.* (%) of brominated compounds Calcd. C	Calcd. H	Found C	Found H	$\bar{n}$
XIIIb	91.47	5.76	—	91.36	5.77	—	38.41	2.42	38.59	2.50	5
XIIIc	92.15	5.80	—	92.17	5.80	—	38.01	2.39	37.28	2.34	7
XIV	81.11	5.99	—	81.06	6.15	—	38.11	2.82	37.04	2.66	7
XV	75.66	4.35	5.75	75.65	4.46	5.53	—	—	—	—	11
XVI	68.21	4.67	4.87	68.18	4.60	3.88	—	—	—	—	5

Furthermore we could isolate some different compounds (X, XIa, XIb, and XII) (Table III) from the each reaction mixture (see the experimental). These compounds did not exhibit the IR spectral absorptions (in KBr) to both carboxaldehyde and triphenylphosphonium group.[14)] Hence these compounds can be clearly deduced to be cyclic olefin type from the

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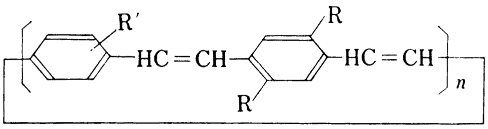
[14)] J.C. Sheldon and S.Y. Tyree, *J. Am. Chem. Soc.*, **80**, 2117 (1958).

data of elementary analysis and mass spectra listed in Table III. As can be seen from the Table III, the cyclic olefins, except compound (X), shows the IR spectral band in the region of *ca.* 960 cm^{-1} (in KBr) assignable to *trans*-1,2-disubstituted olefin. As the ultraviolet (UV) spectra (in 1,2-dichloroethane) of the cyclic olefins do not exhibit a conjugated double bond effect in the each molecular structure, it seems reasonable at present that the molecular configuration may be noncoplanar. However, further studies directed foward the absolute configuration of these compounds (XIa, XIb and XII) are in progress in our laboratory. The absence of IR absorption band (in KBr) of X, attributing to *trans*-1,2-disubstituted olefins, enables to give a deduction to be all *cis*-configuration (Fig. 2). The feature of the NMR spectra (in CCl$_4$) of cyclic compound (X) shows aromatic proton : 7.00 ppm (8H, singlet), 6.62 ppm (4H, singlet); olefinic proton : 6.43 ppm (8H, singlet), and methoxy proton : 3.50 ppm (12H, singlet) (Fig. 3).

Table III. Cyclic Olefins



No.	R	R'	Appearance	mp (°C)	IR KBr (cm^{-1}) $\mathrm{H}{>}\mathrm{C}{=}\mathrm{C}{<}\mathrm{H}$	$\lambda_{max}^{1,2\text{-}C_2H_4Cl_2}$	$\varepsilon \times 10^{-4}$
IX	H	H	—	—a)	—a)	—	—a)
X	OCH$_3$	H	pale yellow prisms	168—170	—	305	3.21
XIa	H	NO$_2$	pale yellow prisms	199—201	970	—	—a)
XIb	H	NO$_2$	yellow prisms	180—184	968	350	6.10
XII	OCH$_3$	NO$_2$	orange prisms	175—180	963	343 413	2.89 3.64

No.	Mass Spectrum M$^+$ (*m/e*)		*Anal.* (%)						*n*
			Calcd.			Found			
	Calcd.	Found	C	H	N	C	H	N	
IX	408 612	408 612	—	—	—	—	—	—a)	2 3
X	528.2301	528.2330	—	—	—	—	—	—a)	2
XIa	498	498	—	—	—	—	—	—a)	2
XIb	747	747	77.09	4.45	5.62	76.82	4.58	5.43	3
XII	618	618	69.89	4.89	5.53	69.54	4.89	5.40	2

a) not measured

Therefore the configuration of compound (X) can be postulated to be a magnetically molecular symmetry on the basis of the NMR spectral data in respect of all singlet protons asmentioned above especially. As may be shown in Fig. 4, therefore it seems conceivable that each plane of four benzene rings must be arranged relatively and alternatively at 90° angle. The molecular model may be supported to be stereochemically one of the most stable configurations.

Finally, we attempted the Wittig reaction of bisphosphonium salt (Ia) or (Ib) with 9,10-anthracenedicarboxaldehyde (XVII) to yield two kinds of the corresponding olefins (XVIIIa and XIXa, or XVIIIb and XIXb), respectively (Chart 3). Elementary analytical data and mass spectra of the olefinic compounds (XVIIIa and XVIIIb) each led to the agreement with

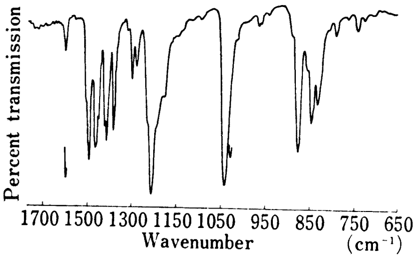


Fig. 2. Infrared Spectrum of Cyclic Compound (X) in KBr

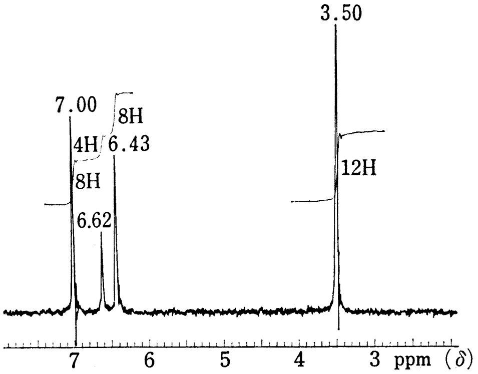


Fig. 3. NMR Spectrum of Cyclic Compound (X) in CCl_4

$C_{40}H_{20}O_2$ and $C_{42}H_{30}O_4$, and the IR spectra (in KBr) indicated at 965 and 980 cm^{-1} the bands assignable to olefinic double bonds, and then the observation of NMR spectra (in dimethylsulfoxide-d_6) gave two-doublets attributable to olefinic protons and coupling constant of 16.5 cps to *trans* configurafon.[11] In support of the above results, the two olefins (XVIIIa and XVIIIb) were consistent with *trans,trans*-1,4-bis[2-(9-formyl-10-anthryl)vinyl]benzene (mp 294—296° : decomp.) and *trans,trans*-1,4-bis[2-(9-formyl-10-anthryl)vinyl]-2,5-dimethoxybenzene (mp>340°), respectively (Table IV).

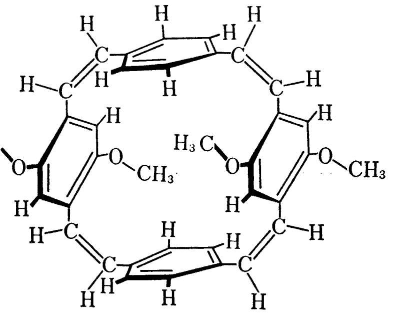


Fig. 4. Structure of Cyclic Compound (X)

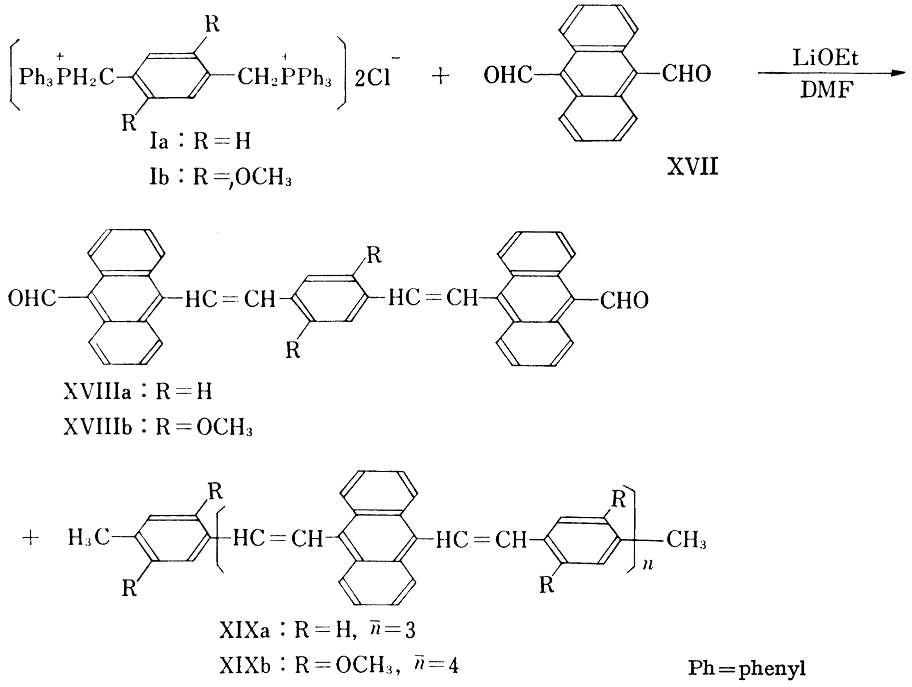
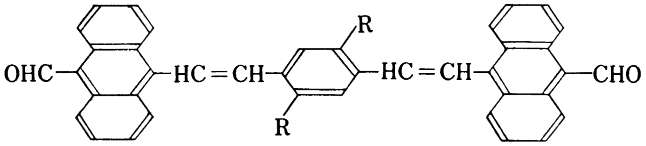


Chart 3

TABLE IV. *trans, trans*-1,4-Bis[2-(9-formyl-10-anthrylene)ethenyl-1]-benzene and *trans, trans*-1,4-Bis[2-(9-formyl-10-anthrylene)ethenyl-1]-2,5-dimethoxybenzene



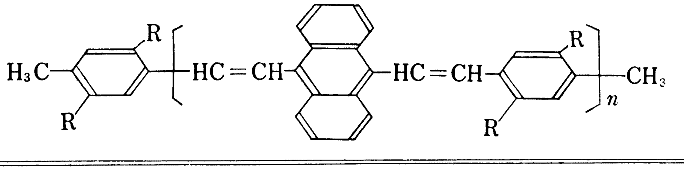
No.	R	Appearance (recryst. solvent)	mp (°C)	Yield[a] (%)	IR $_{\mathrm{KBr}}$ (cm^{-1})	
					$\nu_{C=O}$	$^{H}{>}C{=}C{<}_{H}$
XVIIIa	H	orange prisms (DMF)	294—296 (decomp.)	19	1670	965 957
XVIIIb	OCH_3	reddish orange prisms (xylene)	>340	55	1665	980

No.	Mass Spectrum M^+ (*m/e*)	*Anal.* (%) Calcd.		Found		NMR δ(ppm)[b] (in DMSO-d_6)		
		C	H	C	H	Olefinic proton	*J* (cps)	-CHO proton
XVIIIa	538	89.19	4.87	89.02	5.15	8.15 (d) 7.05 (d)	16.5 16.5	11.33 (s)
XVIIIb	598	84.26	5.05	84.08	5.02	8.24 (d) 7.24 (d)	16.5 16.5	11.57 (s)

[a] calcd. on the basis of Phosphonium Salts (R=H, R=OCH_3), respectively

[b] d: doublet, s: singlet

TABLE V. Apperarance and Analytical Data of



No.	R	Appearance	mp (°C)	IR $_{\mathrm{KBr}}$ (cm^{-1})	
				δ CH_3	$^{H}{>}C{=}C{<}_{H}$
XIXa	H	orange cryst. powder	>340	1440 1370	965
XIXb	OCH_3	reddish orange cryst. powder	>340	1460 1440 1405 1380	970

No.	*Anal.* (%) Calcd.		Found		*Anal.* (%) of brominated compound Calcd.		Found		*n*
	C	H	C	H	C	H	C	H	
XIXa	94.26	5.74	93.27	5.54	48.57	2.96	48.25	2.72	3
XIXb	84.31	5.83	84.47	5.86	47.17	3.26	41.76	2.46	4

Only on the basis of the absence of the IR absorption bands attributable to carboxaldehyde and triphenylphosphonium group, the configurational assingment might give an olefinic ring form to the compounds (XIXa and XIXb). However, in general, the mass spectra of these compounds exhibit very complicated and sometimes unassignable patterns in comparing with that of usual olefinic ring compounds. Describing in details, among the peak-groups detected to *ca.* 1000 and 1100 *m/e*, there were ion peaks to $n=1$ (410 *m/e*) and $n=2$ (714 *m/e*) in the former (XIXa), and in the latter (XIXb), $n=1$ (530 *m/e*), $n=2$ (894 *m/e*), respectively. Unfavorably, however, peaks assignable to the ring formation did not indicated. The average values of the polymerization degree ($\bar{n}$) on the compounds (XIXa and XIXb) could respectively be presumed to be 3 and 4, in terms of the elementary analytical data, and these corresponding bromides, and also the mass spectral data (Table V).

To make more sure the above such probable conclusion, the comparative studies were carried out by the IR and NMR spectral observation of 9,10-bis(4-methylstyryl)anthracene (XX) (mp 287—288°), ($n=1$ of the oligopolymer XIXa), because the structure of XX was same to the unit of XIXa. From the above results, it was confirmed that the IR spectral pattern of compound (XX) was expectedly quite similar to that of XIXa and also the mass spectrum of XX was some resemble to that of XIXa, although there were different points each other in their patterns.

Experimental[15]

Preparation of 2,5-Dimethyoxy-*p*-xylylene-bis(triphenylphosphonium chloride) (Ib)——A solution of 8.5 g (0.036 mole) of 2,5-bis(chloromethyl)hydroquinone dimethylether[9] and 20 g (0.076 mole) of triphenylphosphine in 150 ml of dimethylformamide was refluxed with stirring for 2 hr. The reaction mixture was then allowed to cool to room temperature and colorless crystalline product was washed with dimethylformamide, followed by dry benzene and dried in a vacuum desicator over P_2O_5. This crystalline product was melted at 182—183°, then solidified again, and decomposed at 245°. The dry weight was 29 g (98%). An analytical sample was recrystallized from dimethylformamide and dried in a vacuum tube over P_2O_5 at 190°.

Anal. Calcd. for $C_{46}H_{42}O_2P_2Cl_2 \cdot H_2O$: C, 71.22; H, 5.85. Found: C, 71.26; H, 5.85.

This phosphonium salt remained water of crystallization tenaciously.

IR (KBr) cm^{-1}: 3460 (H_2O), 1107 ($\nu \rangle P^+$–C), 746, 720, 686 ($\nu \rangle P^+$–Ph).

Reactions of Bisphosphorane from Bisphosphonium Salt (Ib) with Benzaldehyde Derivatives and Furfural——General Method: A solution of 4.0 g (0.005 mole) of bisphosphonium salt (Ib) and 1.3 g (0.012 mole) of benzaldehyde in 60 ml of absolute ethanol was stirred at room temperature. To the above solution was added dropwise a solution of 0.07 g (0.01 g atom) of lithium dissolved in ethanol (20 ml). After stirring for 2 hr, 10 ml of water was added and yellow crystalline precipitate formed was filtered to give yellow crystals. To the filtrate was added more 200 ml of water, extracted with benzene which was dried over Na_2SO_4 and the extract concentrated. This benzene solution was adsorbed to a column of silicagel and eluted with benzene to give yellow crystals. Combined crystals (*cis-trans* mixture) were recrystallized from boiling benzene in the presence of a trace of iodine to give pure *trans*, *trans*-1,4-distyryl-2,5-dimethoxybenzene (II), as green-yellow needles, mp 190—190.5°.

The other reactions were carried out as above, but exceptionally, separation of *cis*, *trans* isomers from the crude 1,4-bis(4-nitrostyryl)-2,5-dimethoxybenzene (IV) with fractional recrystallization from a benzene–chloroform mixture gave two isomers of *cis*, *cis*-1,4-bis(4-nitrostyryl)-2,5-dimethoxybenzene (IVa), mp 230° and *trans*, *trans*-1,4-bis(4-nitrostyryl)-2,5-dimethoxybenzene (IVb), mp 301°.

Appearance, melting point, yield and analytical and spectral data were listed in Table I.

Reaction of Bisphosphorane from *p*-Xylylene-bis(triphenylphosphonium chloride)[6] (Ia) with Terephthalaldehyde (VIIIa)——To a solution of 14 g (0.02 mole) of bisphosphonium salt (Ia) and 2.65 g (0.02 mole) of terephthalaldehyde (VIIIa) in 200 ml of ethanol was dropwise added a solution of 0.28 g (0.04 g·atom) of lithium dissolved in 50 ml of ethanol with stirring under nitrogen over a period of 5 hr. The point of contact assumed a deep reddish orange color and on mixing, yellow precipitate formed, which was filtered, washed with ethanol and dried *in vacuo* to give 4.48 g (quantitative) of yellow crystalline powder, mp >340°.

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15) *a*) All melting points were not corrected; *b*) The spectrometers used in this work were as follows, IR spectrum: Nihonbunko Model-DS301 infrared spectrophotometer, NMR spectrum: Nihondenshi Model-C-60H NMR Spectrometer (60 MHz, TMS as the internal reference), mass spectrum: Nihondenshi Model-JMS-O1SG Mass Spectrometer (75 eV, as an ionization potential).

The ethanol filtrate gave 10.2 g (97%) of triphenylphosphine oxide. The yellow crystalline powder obtained was extracted with benzene by a soxhlet extractor to remove lower molecular weight fraction. The remainder was recrystallized from dimethylformamide to give the poly-*p*-xylylidene, XIIIb (mp >340°).

Reaction of compound (XIIIb) suspended in carbon tetrachloride with bromine gave a colorless solid, primarily saturated, brominated analog of XIIIb, $C_{88}H_{66}O_2Br_{20}$. Additionally, the mass spectrum of lower molecular weight fraction which was extracted with benzene indicated a presence of cyclic compound (IX: $n=2$ and 3) (Table III).

On the other hand, the similar reaction of bisphosphonium salt (Ia) with bisaldehyde (VIIIa) in dimethylformamide gave the poly-*p*-xylylidene (XIIIc) which was somewhat higher molecular weight than XIIIb.

The infrared spectrum showed the presence of unsaturation and carboxaldehyde group, but no band attributable to the phosphonium group was observed. Appearance and analytical data were shown in Table II.

Reaction of Bisphosphorane from 2,5-Dimethoxy-*p*-xylylene-bis(triphenylphosphonium chloride) (Ib) with Terephthalaldehyde (VIIIa)——To a solution of 8.0 g (0.01 mole) of bisphosphonium salt (Ib) and 1.3 g (0.01 mole) of VIIIa in 200 ml of dimethylformamide was added a solution of 0.15 g (0.02 g atom) of lithium dissolved in 30 ml of ethanol as the above conditions. After stirring for 10 hr, the yellowish orange mixture was added 350 ml of 30% ethanol and orange precipitate formed which was filtered, washed with ethanol and dried *in vacuo* to give 2.0 g (quantitative) of orange crystalline solid. This crystalline solid was extracted with benzene and reprecipitated from hot benzene with ethanol several times to give the poly-*p*-xylylidene series (XIV), as orange crystalline powder, mp *ca.* 170°. Infrared spectral data and analytical data were listed in Table II. While, the filtrate was added more water and extracted with benzene. This benzene extract was dried over Na_2SO_4 and removed benzene to give yellow crystalline solid, which was extracted with ethanol to remove triphenylphosphine oxide. The ethanol solution extracted gave 5.0 g (95%) of triphenylphosphine oxide. The above yellow crystalline solid was dissolved in benzene and adsorbed to silicagel column which was eluted with benzene. The first fraction gave about 20 mg of pale yellow prisms, which was recrystallized from cyclohexane to give pale yellow prisms of cyclic compound (X), mp 168—170°.

Analytical data were shown in Table III. Infrared spectrum was shown in Fig. 2 and NMR spectrum in Fig. 3.

Reaction of Bisphosphorane from Bisphosphonium Salt (Ia) with 2-Nitroterephthalaldehyde (VIIIb)——The reaction was carried out as above and the reddish orange mixture was added 20 ml of water. The orange precipitate formed, which was filtered, washed with ethanol and dried to give 1.3 g of orange crystalline solid (compound A). The filtrate was added more 200 ml of water and extracted with chloroform. This chloroform extract was dried over Na_2SO_4, removed chloroform and extracted with ethanol to give 1.2 g of yellowish orange powder (compound B). The ethanol extract gave 4.8 g (87%) of triphenylphosphine oxide.

The compound A was extracted with hot benzene to remove relatively lower molecular weight fraction and reprecipitated from hot dimethylformamide with ethanol several times to give the poly-*p*-xylylidene series (XV), as reddish orange crystalline powder. Analytical data were shown in Table II.

While, the compound B which was dissolved in chloroform was adsorbed to a column of alumina and eluted with chloroform. The first fraction gave pale yellow prisms of cyclic compound (XIa) and the second fraction gave a trace of yellowish prisms of cyclic compound of XIb. In the infrared spectra of these compounds, no band attributable to the carboxaldehyde group and triphenylphosphonium group was observed, however, the presence of unsaturation was observed. Appearance, melting point and analytical data of these compounds were shown in Table III.

Reaction of Bisphosphorane from Bisphosphonium Salt (Ib) with 2-Nitroterephthalaldehyde (VIIIb)——The reaction was carried out as above. The reddish orange reaction mixture was added 100 ml of water and reddish orange precipitate formed which was filtered, washed with ethanol and dried *in vacuo* to give 2.7 g of reddish orange crystalline powder. A part of this crystalline powder which was dissolved in 1,2-dichloroethane was adsorbed to a column of silicagel and eluted with 1,2-dichloroethane. The first fraction was concentrated and added a small amount of ethanol . The orange precipitate formed was filtered and reprecipitated from 1,2-dichloroethane with ethanol to give a trace of cyclic compound (XII), as an orange prisms. Infrared spectrum of this compound showed neither band of carboxaldehyde group nor triphenylphosphonium group. Analytical data were shown in Table III. Additionally, reddish orange crystalline powder obtained originally was extracted with benzene to remove relatively lower molecular weight fraction and reprecipitated from hot 1,2-dichloroethane with ethanol several times to give the poly-*p*-xylylidene series (XVI), as a reddish orange crystalline powder, mp *ca.* 190°. Appearance and analytical data were shown in Table II.

Reaction of Bisphosphorane from Bisphosphonium Salt (Ia) with 9,10-Anthracenedicarboxaldehyde (XVII)——To a solution of 7.0 g (0.01 mole) of bisphosphonium salt (Ia) and 2.35 g (0.01 mole) of 9,10-anthracenedicarboxaldehyde (XVII)[8] in 200 ml of dimethylformamide was added dropwise a solution of 0.15 g (0.02 g·atom) of lithium dissolved in 30 ml of ethanol over a period of 5 hr. After stirring for 2 hr, the resulting reaction mixture was allowed to stand at room temperature for one night. The orange precipitate formed was filtered which was washed with ethanol, followed by benzene and dried *in vacuo* to give 3.0 g of orange crystalline powder, mp >340°.

The dimethylformamide-soluble part (about 30%) of this crystalline powder was recrystallized from dimethylformamide several times to give pure *trans*, *trans*-1,4-bis[2-(9-formyl-10-anthryl)vinyl]benzene (XVIIIa), mp 294—296° (decomp.). Analytical data were shown in Table IV.

Additionally, the dimethylformamide-insoluble residue was washed with hot dimethylformamide, followed by hot dimethylsulfoxide to give insoluble oligopolymer (XIXa), as an orange crystalline powder, mp>340°. Infrared spectrum of this oligopolymer showed neither band of carboxaldehyde group nor triphenylphosphonium group, but the presence of unsaturation. The mass spectrum, which was very complicate pattern, showed the molecular ion peaks attributable to the lower molecular weight series of oligopolymer XIXa, 410 *m*/e ($n=1$) and 714 *m*/e ($n=2$), and fragment ion peak more than *ca.* 1000 *m/e*. Analytical data were shown in Table V.

Reaction of Bisphosphorane from Bisphosphonium Salt (Ib) with Bisaldehyde (XVII)——The similar reaction as above gave 2.2 g of reddish orange crystalline solid. The fractional recrystallization of this compound from dimethylformamide gave two kinds of crystals which were reddish orange prisms and reddish orange crystalline powder in the ratio 5:1. The former was recrystallized from xylene to give pure *trans*, *trans*-1,4-bis[2-(9-formyl-10-anthryl)vinyl]-2,5-dimethoxybenzene (XVIIIb), mp>340°. Analytical data were shown in Table IV.

While, the latter was recrystallized from dimethylformamide again to give reddish orange oligopolymer (XIXb), mp >340°. Infrared spectrum showed the presence of unsaturation. No bands attributable to the carboxaldehyde group and triphenylphosphonium group were observed. Mass spectrum showed the molecular ion peak attributable to the lower molecular weight series of XIXb, 530 *m/e* ($n=1$) and 894 *m/e* ($n=2$), and fragment ion peak more than 1100 *m/e*. No peaks attributable to the highest molecular ion and cyclic molecular ion were observed. Analytical data were shown in Table V.

Preparation of 9,10-Bis(4-methylstyryl)anthracene (XX)——To a solution of 2.0 g (0.005 mole) of 4-methylbenzyltriphenylphosphonium chloride[16] and 0.6 g (0.0025 mole) of 9,10-anthracenedicarboxaldehyde (XVII) in 150 ml of dimethylformamide was added dropwise a solution of 0.04 g (0.005 g atom) of lithium dissolved in 10 ml of ethanol. After stirring for 3 hr, to the reaction mixture was added 300 ml of ethanol. The yellow crystalline solid formed was filtered and dried *in vacuo* to give 0.8 g (80%) of crude 9,10–bis(4-methylstyryl)anthracene. The crude product was recrystallized from boiling benzene in the presence of trace of iodine to give pure *trans*, *trans*-9,10-bis(4-methylstyryl)anthracene, as a yellow prisms, mp 287—288°.

Anal. Calcd. for $C_{32}H_{26}$: C, 93.62; H, 6.38. Found: C, 93.54; H, 6.46.

IR (KBr) cm^{-1}: 1440, 1370 (δ CH_3), 970 (*trans* -CH=CH-).

NMR (in $CDCl_3$) ppm (δ): 7.83, 6.84 (4H, two-doublet, $J=16$ cps, olefinic proton), 2.41 (6H, singlet, CH_3).

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[16] G. Drefahl and G. Plötner, *Chem. Ber.*, **93**, 990 (1960).