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Cyclic Acetylenes. XI. The Syntheses of *p,p′*-Bridged Cyclic Tolans by the Fritsch-Buttenberg-Wiechell Rearrangement[1]

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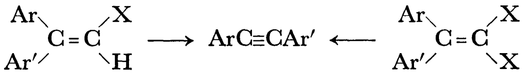
In order to ascertain the effect of ring strain on the electronic spectra of cyclic acetylenes, a series of *p,p′*-bridged cyclic tolans (V_n, $n=11$, 12, 13, 14, and 18) has been synthesized. It was found that the increasing ring strain exerted an appreciable hypochromic effect and also caused a slight bathochromic shift of the absorption band. The bathochromic shift observed in the *p,p′*-bridged cyclic tolans (V_n) forms a contrast with the hypsochromic shift observed in the strained *o,o′*-bridged cyclic diphenyldiacetylene (VI, $n=3$).

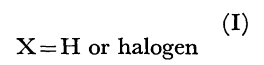
The formation of diarylacetylene from 1,1-diaryl-2-haloethylene by dehydrohalogenation, accompanied by rearrangement, has been well-known as the Fritsch-Buttenberg-Wiechell rearrangement.[2] The treatment of 1,1-diaryl-2,2-dihaloethylene with an organometallic compound also results in the formation of diarylacetylene.[3,4]



$$\mathrm{(Ar)(Ar')C{=}C(X)(H)} \longrightarrow \mathrm{ArC{\equiv}CAr'} \longleftarrow \mathrm{(Ar)(Ar')C{=}C(X)(X)}$$

X = halogen

If a diarylhalo- or a diaryldihaloethylene in which the aryl groups are linked by a bridging chain (R) is subjected to the above-mentioned rearrangement, we can expect the formation of a cyclic diarylacetylene with a bridging chain between the aryl groups (I). As the distance between the *p*- and *p′*-positions of the two aryl groups in the ethylene is shorter than that of in the cyclic acetylene, the rearrangement reaction seems to offer a method of synthesizing highly-strained cyclic acetylene. Also, the rearrangement reaction in which the aryl group migrates with a bridging chain seems to be of interest in itself. An analogous



(I)

X = H or halogen
Y = halogen

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[1] This paper is dedicated to Professor Munio Kotake in commemoration of his seventy-fifth birthday by one of his former students (M. N.).

[2] P. Fritsch, *Ann.*, **279**, 319 (1894); W. Buttenberg, *ibid.*, **279**, 324 (1894); H. Wiechell, *ibid.*, **279**, 337 (1894).

[3] D. Y. Curtin and E. W. Flym, *J. Amer. Chem. Soc.*, **81**, 4714 (1959).

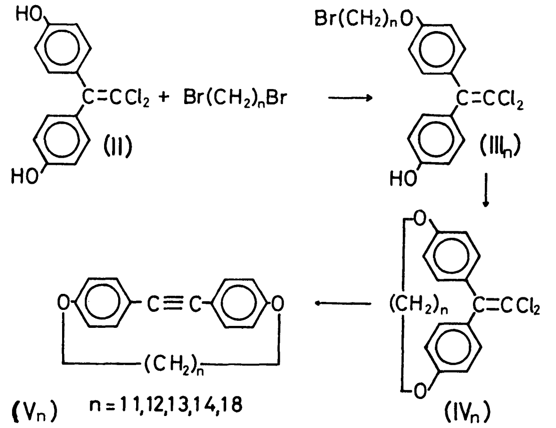
[4] B. Kirby, W. G. Kofron, and C. R. Hauser, *J. Org. Chem.*, **28**, 2176 (1963).

[5] G. Wittig, W. Joos, and P. Rathfelder, *Ann.*, **610**, 180 (1957); G. Wittig and J. G. Grolig, *Chem. Ber.*, **94**, 2148 (1961).

type of rearrangement has been studied by Wittig[5] in the case of the benzidine rearrangement of *N,N'*-polymethylene hydrazobenzenes.

The present paper will deal with the syntheses of polymethylene ether derivatives of *p,p'*-dihydroxytolan according to the Fritsch-Buttenberg-Wiechell rearrangement reaction.

Syntheses. 1,1-Dichloro-2,2-bis(*p*-hydroxyphenyl)-ethylene,[6] which had been derived from 1,1,1-trichloro-2,2-bis(*p*-hydroxyphenyl)ethane,[7] was treated with a large excess of polymethylene dibromide in the presence of potassium hydroxide to yield the monoether III.[8] The intramolecular alkylation of the monoether III to yield the cyclic ether derivative IV was achieved by the Lüttringhaus method[8] under highly diluted conditions. The monomeric nature of IV was confirmed by a molecular weight determination according to the Rast method. The reaction conditions, the yields, and the melting points of IV are summarized in Table 1. The decreasing yields of the cyclic ethers IV with the diminishing length of the bridging chain clearly indicate the increasing difficulty of the intramolecular alkylation with the shorter chain.



Generally, the rearrangement reaction was carried out in an ether solution by treating IV_n with a 10% excess of *n*-butyllithium at a temperature of —17—−18°C for 1 hr. In the case of IV_{14}, a 100% excess of *n*-butyllithium was employed. Also, in the case of IV_{18}, the dichloroethylene was treated with a 100% excess of *n*-butyllithium at 2°C for 1 hr, and then at 18°C for 1 hr. The yields and the melting points of the cyclic tolans (V_n) are tabulated in Table 2, along with those of the reference substance, 4,4'-di-*n*-butoxytolan.

Table 1. The intramolecular alkylation of III_n

n	III (mmol)	Reaction time (hr)	IV mp (°C)	IV Yield (%)
10	8.0	65	134.2—135.6	39
11	20.6	69	127.5—128.5	46
12	9.2	29	128.0—129.2	49
13	12.0	37	78.0— 78.8	60
14	9.0	40	89.5— 91.5[a] 83.1— 84.0	60
18	7.9	30	90.0— 91.0	94
		n-Bu	76.0— 77.0	

a) Dimorphism.

In the case of IV_{10}, the cyclic tolan (V_{10}) could not be obtained. The amorphous yellow solid which was isolated from the reaction product seemed to be a complex mixture and could not be identified. The colorless crystals of V_{11} and V_{12} were found to be rather unstable. On exposure to a diffused light in the laboratory, the formation of a violet-colored layer on the surface of the crystals of V_{11} and V_{12} was observed. On the other hand, the cyclic tolans of the higher ring member, V_{13-18}, and the open-chain analogue were found to be stable compounds. The tendency toward sublimation observed in V_{12}, V_{13} and V_{14} seems to reflect the rigid structures of these molecules with a tightly-drawn polymethylene bridge.

Table 2. The yields and the melting points of V_n

n	Yield (%)	Mp (°C)	Recovered IV_n(%)
10	0	—	29
11	23	166.0—167.0	46
12	47	151.0—152.0	49
13	75	158.5—159.5[a] 160.0—161.2	20
14	90	167.3—168.3	0
18	75	118.4—119.0	0
n-Bu	52	130.5—131.5	43

a) Dimorphism.

It is difficult to reach a definite conclusion from the results of the rearrangement reactions, as the reactions were carried out under different conditions. However, as it has been proved that the presence of a large excess of *n*-butyllithium had no influence on the rearrangement reaction,[3] it seems to be evident that the diminishing length of the bridging chain retards the rearrangement or enhances some side reactions, resulting in a decrease in the yields of the cyclic acetylenes. However, it should be noted that a much higher yield than that of the open-chain analogue was obtained in the case of $n=14$[9] Either the fixation of the phenyl groups in IV_{14} in a favorable position for the rearrangement, resulting from the presence of the bridging chain in an adequate length, or the increased intramolecular nature of the reaction brought about by the linking of the migrating moiety, seemed to be the cause of the high yield of V_{14}.

Electronic Spectra. The electronic spectral data of 1,1-dichloro-2,2-bis(*p*-hydroxyphenyl)ethylene polymethylene ethers (IV_n) are summarized in Table 3, together with those of the open-chain reference. Slight

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[6] H. Hubacher, *J. Org. Chem.*, **24**, 1949 (1959).

[7] H. P. Kaufmann and J. Schierholt, *Pharm. Zentralhalle*, **96**, 443 (1957); *Chem. Abstr.*, **52**, 13686 (1958).

[8] A. Lüttringhaus, *Ann.*, **528**, 211 (1937); A. Lüttringhaus and K. Ziegler, *ibid.*, **528**, 155(1937); K. Ziegler, A. Lüttringhaus, and K. Wohlgemuth, *ibid.*, **528**, 162 (1937).

[9] An analogous result was obtained in the case of the synthesis of *o,p'*-bridged cyclic tolans by the same rearrangement. See the following paper.

TABLE 3. THE ELCTRONIC SPECTRAL DATA OF IV_n IN n-HEXANE

IV_n	$\lambda_{\max}$ in mμ (ε)	
n=10	255.5(18,300)	277*(15,100)
11	254 (17,700)	276*(14,700)
12	255 (19,100)	275*(16,900)
13	254 (19,800)	275*(16,700)
14	254 (20,500)	275*(16,900)
18	254 (20,300)	275*(15,800)
n-Bu	254 (21,300)	275 (15,900)

The asterisks indicate the inflexions.

bathochromic and hypochromic effects were observed with a decrease in the ring size. A similar, but a more appreciable, spectral trend has been found in the case of [1,n]paracyclophanes and has been explained in terms of a transannular electronic coupling of the two phenyl groups and a modification of the benzenoid resonance due to the bending of the two benzene nuclei.[10] However, in the case of IV_n, the cross-conjugation of the phenyl groups with the dichloromethylene group and the interaction of the phenyl groups with the lone-pair electrons in the oxygen atoms in the ether linkages may be altered by the change in the ring size. Because of these situations, it seems to be difficult to deduce a definite correlation between the spectral behavior and the ring size of IV_n.

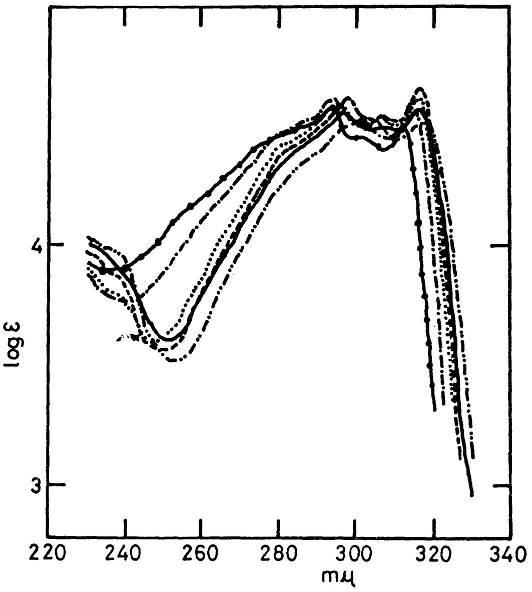


Fig. 1. The electronic spectra of V_n and p,p'-dibutoxytolan

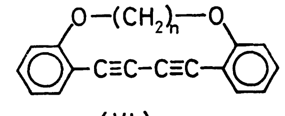
n=11 -··-··- 14 ·········
12 ——— 18 -·-·-·
13 -------- n-Bu —•—•—

Figure 1 and Table 4 record the absorption curves and the data of the cyclic tolans (V_n) along with those of p,p'-dibutoxy-diphenylacetylene as a reference compound.

TABLE 4. THE ELECTRONIC SPECTAL DATA OF V_n IN n-HEXANE

V_n	$\lambda_{\max}$ in mμ (ε)		
n=11	300 (33,700)		318 (33,400)
12	298 (37,000)	308 (31,400)	317 (36,900)
13	297.5(42,300)	307 (34,800)	317 (44,300)
14	297 (42,300)	306.5(35,300)	316 (42,600)
18	295.5(41,700)	305 (33,500)	315 (35,500)
n-Bu	294 (37,700)	303 (29,200)	313 (31,900)

It will be seen that the ring formation causes an increase in the absorption intensity. The maximum intensity was observed in V_{13}. However, the absorption intensity decreased with a decrease in the number of n, accompanied by a slight bathochromic shift of $\lambda_{\max}$. The increase in the absorption intensity can be rationalized by the increased coplanarity of the phenyl groups caused by the ring formation. On the other hand, the regular red shift of the $\lambda_{\max}$ with the diminishing ring size and the decrease in the extinction coefficient going from V_{13} to V_{11} seems to be attributable to the effect of strain on the electronic spectra. The bathochromic shift observed in V_n makes a sharp contrast with the hypsochromic shift observed in a strained diphenyldiacetylene derivative (VI, n=3).[11]



(VI)

Infrared Spectra. The 1580-cm^{-1} absorption band due to the skeletal in-plane vibration of an aromatic ring conjugated with the lone-pair electrons in a substituent, which could be observed in the spectrum of V_{18} at 1569 cm^{-1}, was found to be extremely weak in other members of V_n. This fact seems to indicate that the polymethylene bridge (n=11—14) would cause a fixation of the conformation of the oxygen atom at a position unfavorable for the conjugation with the aromatic ring. A regular shift of the absorption band due to the skeletal in-plane vibration of a benzene nucleus (*ca.* 1600 cm^{-1}) toward a lower wavenumber with a decrease in the ring size was observed; *i. e.*, the band appearing at 1609 cm^{-1} in the spectrum of V_{18} moved to 1596 cm^{-1} in that of V_{11}. Also, the fact that the spectra of V_{11} and V_{12} exhibit sharper absorption peaks than those of the other higher homologues seems to indicate the limited mode of vibration resulting from the fixed conformation and rigid structure of V_{11} and V_{12}. The characteristic peaks in the IR spectra of V_n are tabulated in Table 5, together

TABLE 5. THE IR SPECTRA OF V_n (cm^{-1})

V_n	$\nu_{C=C}$ (arom.)		δ_{C-H} (arom.)	
11	1596	1561(w)	832(s)	
12	1600(s)	—		843(s)
13	1605(s)	—	830(s)	
14	1605(s)	—		836(s)
18	1609(s)	1569(m)	831(s)	836(s)
n-Bu	1611(s)	1571(m)	830(s)	848(s)

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[10] D. J. Cram and M. F. Antar, *J. Amer. Chem. Soc.*, **80**, 3103 (1958).

[11] F. Toda and M. Nakagawa, This Bulletin, **34**, 862 (1961).

with that of the open-chain analogue, *p,p'*-dibutoxytolan.

Nuclear Magnetic Resonance Spectra. The most characteristic feature of the NMR spectra of V_n is the presence of strong and rather sharp peaks centered around 9 τ, as is illustrated in Fig. 2. The most well-defined spectrum was obtained in V_{12}, and the triplet at 5.82 τ changed to a sharp singlet on the irradiation of the peak at 8.45 τ. On the basis of this finding, the triplet centered at 5.82 τ and 8.45 τ can be assigned to the protons of the α- and β-methylene groups of the oxygen atom respectively.[12] Therefore, the peak at 9.29 τ should be attributed to the protons of the other methylene groups. The aromatic nuclei and the triple bond should exert shielding[13] and deshielding effects[14] on the protons situated just on these structural units. However, the observed spectra indicate that an almost uniform magnetic environment is attained in the vicinity of the *p,p'*-disubstituted tolan system. This fact seems to be difficult to understand at first sight; however, the change in the electronic state caused by the conjugation of the phenyl nuclei with the triple bond may be responsible for the formation of the uniform magnetic environment.[15] The low-field shift of the peaks as compared with those of 4,4'-polymethylene biphenyls[16] seems to reflect the effect of acetylenic linkage.

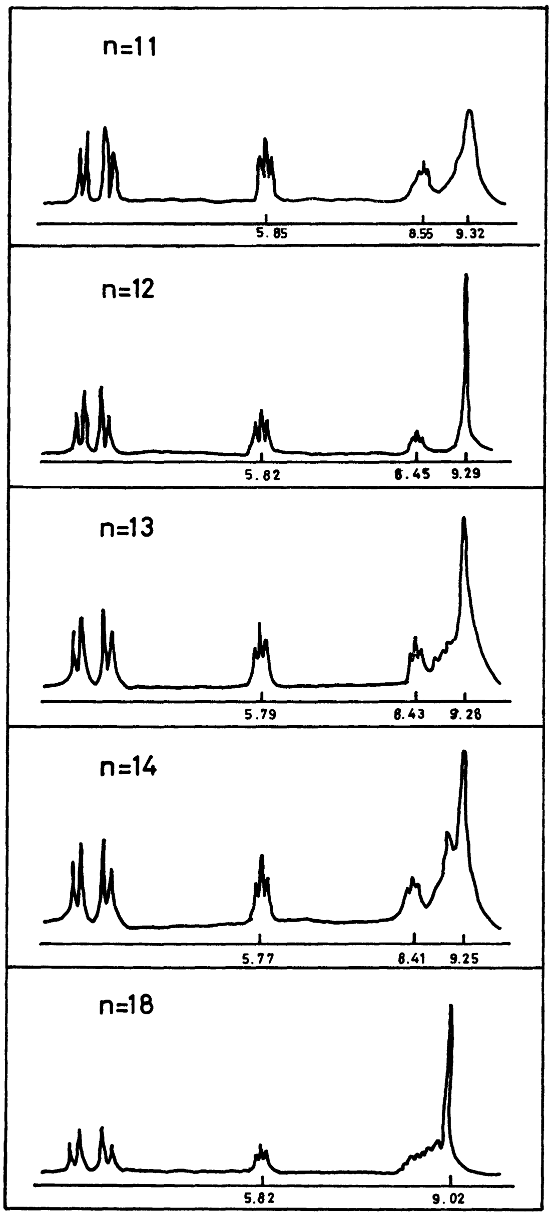

Fig. 2. The NMR spectra of V_n.

Experimental

All the melting points are uncorrected. The infrared spectra were measured with a Hitachi EPI-2 Spectrophotometer by the KBr-disk method, the electronic spectra, with a Hitachi EPS-2 Spectrophotometer, and the NMR spectra, with a Varian A 60 Spectrometer.

*1,1-Dichloro-2,2-bis(*p*-hydroxyphenyl)ethylene (II).* 1,1,1-Trichloro-2,2-bis(*p*-hydroxyphenyl)ethane[7] was treated potassium hydroxide in methanol according to the reported method,[6] yielding II in a yield of 66.8%.

1,10-Dibromodecane. A commercial product was used.

1,11-Dibromoundecane. 10-Undecenol was prepared by the lithium aluminum hydride reduction of ethyl 10-undecenoate.[17] The acetate of 10-undecenol in benzene was treated with hydrogen bromide in the presence of benzoyl peroxide under the irradiation of UV light, thus affording 11-bromoundecanol acetate in a yield of 85%.[18] The hydrolysis of the bromo-acetate by means of potassium hydroxide in methanol resulted in the formation of a mixture of 11-bromoundecanol and 1,11-undecanediol (*ca.* 1 : 1), accompanied by a small amount of 11-undecenol. After the removal of the olefin under reduced pressure, hydrogen bromide was passed through the molten mixture of the alcohols at 130°C.[19] 1, 11-Dibromoundecane was obtained as a colorless liquid (bp 145—148°C/3 mmHg) in a yield of 81%.

1,12-Dibromododecane. Ethyl undecenoate[17] was converted to ethyl 11-bromoundecanoate according to the known method.[18] A mixture of the bromoester (350 g, 1.19 mol), powdered potassium cyanide (220 g, 3.38 mol), potassium iodide (5 g), cupric sulfate monohydrate (1 g), ethanol (1300 m*l*), and water (400 m*l*) was then refluxed for 8 hr. The crude ethyl 11-cyanoundecanoate obtained by working up the reaction mixture by an ordinary method was refluxed for 2 hr in a mixture of acetic acid (250 m*l*) and concentrated sulfuric acid (250 m*l*). The cooled reaction mixture was poured into ice water (3 *l*), yielding crude 1,12-dodecanedioic acid (251 g). The diethyl ester (241.4 g, 0.84 mol) which had been prepared from the crude dioic acid according to the usual

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[12] The double-resonance measurement was performed on a nuclear magnetic resonance spectrometer, C-60 of the Japan Electron-Optics Laboratory Co., Ltd. The authors wish to thank Professor Toshio Miwa, Department of Chemistry, Faculty of Science, Osaka City University, for the measurement and for his helpful advice.

[13] C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958); J. S. Waugh and R. W. Fassenden, *J. Amer. Chem. Soc.*, **79**, 846 (1957).

[14] H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957).

[15] The same type of NMR spectra was obtained in the case of the polymethylene ether derivatives of 4,4'-dihydroxydiphenyldiacetylene. These results will be published in the near future.

[16] M. Nakazaki and K. Yamamoto, *Chem. Ind.* (London), **1965**, 486.

[17] G. H. Jeffery and A. I. Vogel, *J. Chem. Soc.*, **1948**, 658.

[18] *Cf.* R. Huisgen, H. Walz, and I. Glogger, *Chem. Ber.*, **90**, 1437 (1957).

[19] *Cf.* W. L. McEwen, "Organic Syntheses," Coll. Vol. III, p. 227 (1955).

method[20] was reduced by means of lithium alminum hydride to yield 1,12-dodecanediol[21] (159.9 g, 93.8%). The method used in the preparation of 1,11-dibromoundecane was used for the conversion of the diol (203.3 g, 1 mol) to 1,12-dibromododecane (248.6 g, 75.8%).

1,13-Dibromotridecane. 1,13-Tridecanedioic acid was prepared by the reaction of ethyl 11-bromoundecanoate (390.3 g, 1.33 mol) and diethyl sodiomalonate according to the reported method.[22] The crude diacid thus obtained was converted to the diethyl ester[20]; bp 159.0—163.0°C/2.7 mmHg, 295.8 g (74% based on the bromoundecanoate). The lithium alminum hydride reduction of the diethyl ester afforded 1,13-tridecanediol.[21] 1,13-Dibromotridecane, bp 162—164°C/3 mmHg, was obtained from the diol according to the above-stated method[19] in a yield of 59.8% (based on diethyl tridecanoate).

1,14-Dibromotetradecane. 1,12-Dibromododecane (164 g, 0.5 mol) was converted to crude 1,14-tetradecanedioic acid (126 g) *via* 1,12-dicyanododecane according to the method in the literature.[23] The diethyl ester derived from the dioic acid[20] was reduced to 1,14-tetradecanediol by means of lithium aluminum hydride.[21] 1,14-Dibromotetradecane was obtained from the diol in a yield of 57% (based on the diethyl ester) by treating it with hydrogen bromide at 130°C.[19]

1,18-Dibromooctadecane. Dimethyl octadecanedioate was prepared by the electrolysis of methyl hydrogen sebacate.[24] The lithium alminum hydride reduction of the dimethyl ester according to the above-described procedure[21] afforded 1,18-octadecanediol in a yield of 89%. The reaction of hydrogen bromide[19] with the diol at 120—135°C yielded 1,18-dibromooctadecane, bp 175—180°C/0.005 mmHg; mp 54—58°C, in a yield of 61%.

*Preparation of ω-Bromoalkyl Ether of 1,1-Dichloro-2,2-bis(*p*-hydroxyphenyl)ethylene (III$_{10-13}$).* The synthesis of ω-bromodecyl ether (III$_{10}$) will be described as a representative example. To a stirred and refluxing mixture of the bisphenol (II, 12.2 g, 0.0436 mol), anhydrous ethanol (100 m*l*), and 1,10-dibromodecane (91.5 g, 0.279 mol), we added 16.2 m*l* (0.0218 mol) of a 1.34N solution of potassium hydroxide in ethanol over a period of 15 min. The reaction mixture showed pH 5 after having been refluxed for a further 15 min. The cooled reaction mixture was then poured into water (300 m*l*) and extracted with ether. The extract was washed successively with water and a sodium hydrogen carbonate solution, and dried. After the solvent had been removed under reduced pressure, the excess of the dibromodecane was recovered by vaccum distillation under a nitrogen atmosphere (bp 131—137°C/3.7 mmHg, 80.6 g). The residue in benzene was chromatographed on alumina (300 g). The first fraction, on evaporation, gave a small amount of the dibromodecane. A minor amount of the substance obtained from the second fraction seemed to be 1,1-dichloro-2,2-bis(*p*-10-bromodecanoxyphenyl)ethylene; however, further investigation of this substance was not carried out. The crude mono-ether (III$_{10}$) which was obtained from the third fraction as a yellow waxy solid was rechromatographed on alumina to afford colorless III$_{10}$ in a yield of 41.2% (based on the potassium hydroxide). This was used for the following reaction. The bisphenol (II) was recovered from the final fraction.

The other mono-ethers (III$_{11}$, III$_{12}$ and III$_{13}$) were obtained according to the procedure described above. The yields may be summarized as follows: III$_{11}$: 22%; III$_{12}$: 33.3%; III$_{13}$: 34.7%.

Preparation of the Higher ω-Bromoalkyl Ether of the Dichloroethylene (III$_{14}$ and III$_{18}$). Considering the high boiling and high melting points of 1,14-dibromotetradecane and 1,18-dibromooctadecane, the procedure of the recovery of the dibromoalkanes was slightly modified. After the reaction mixture had been mixed with water, the precipitated solid was repeatedly extracted with petroleum ether. The evaporation of the solvent then gave the crude dibromoalkanes. A material insoluble in petroleum ether was taken up in ether, and the aqueous layer was extracted with ether. The combined ethereal extracts were washed successively with water and a sodium hydrogen carbonate solution, and were then dried and evaporated under reduced pressure. The residue was combined with the distillation residue of the above-mentioned crude dibromoalkane and chromatographed on alumina to afford III$_{14}$ (42%) and III$_{18}$ (52%).

Synthesis of the Cyclic Ethers (IV$_n$). As all the intramolecular alkylations of III$_n$ were carried out under almost the same conditions, the procedure employed for the preparation of IV$_{10}$ will be described as a typical example. A solution of the mono-ether (III$_{10}$, 4.00 g, 0.008 mol) in isoamyl alcohol (250 m*l*) was added slowly to a vigorously-stirred and refluxing mixture of anhydrous potassium carbonate (3.3 g, 0.024 mol) and isomyl alcohol (300 m*l*) over a period of 65 hr, employing a high-dilution apparatus. After further refluxing for 2.5 hr, the cooled reaction mixture was filtered to remove any inorganic material. The yellowish-brown residue obtained by evaporating the solvent under reduced pressure was then redissolved in ether and washed thoroughly with a 10% aqueous solution of sodium hydroxide and water successively. The filtered ether solution was dried. The subsequent evaporation of the solvent resulted in a yellowish-brown liquid which crystallized on standing. The crude material was chromatographed on alumina, thus affording IV$_{10}$ as light yellow crystals (1.3 g, 39.1%). The crystals were purified by rechromatography on alumina and by recrystallization from *n*-hexane to yield pure, colorless IV$_{10}$.

The reaction conditions of the intramolecular alkylation and the melting points and yields of IV$_n$ are summarized in Table 1. Also, the electronic spectral data are recorded in

Table 6. The solvents of recrystallization, the analytical data, and the molecular weights of IV$_n$ and the reference substance

IV$_n$	Solvent		Analytical data (%)			Mol wt
			C	H	Cl	
n=10	*n*-hexane	Found	68.58	6.63	17.04	431
		Calcd	68.73	6.73	16.91	419
11	ethyl acetate	Found	69.04	6.83	16.22	418
		Calcd	69.28	6.98	16.36	433
12	ethyl acetate-	Found	69.66	7.18	15.55	499
	methanol	Calcd	69.79	7.21	15.85	447
13	ethyl acetate-	Found	70.12	7.39	15.27	442
	methanol	Calcd	70.27	7.34	15.37	461
14	ethyl acetate-	Found	70.79	7.62	15.05	515
	methanol	Calcd	70.73	7.63	14.91	476
18	petroleum	Found	72.46	8.47	13.15	480
	benzine	Calcd	72.30	8.34	13.34	531
n-Bu	ethanol	Found	67.08	6.61	17.90	
		Calcd	67.18	6.66	18.03	

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[20] *Cf.* V. M. Microvic, "Organic Syntheses," Coll. Vol. II, p. 264 (1943).

[21] *Cf.* W. H. Huber, *J. Amer. Chem. Soc.*, **73**, 2730 (1951).

[22] F. Kraft and R. Selidis, *Ber.*, **33**, 3571 (1900); J. Walker and J. S. Lumsden, *J. Chem. Soc.*, **79**, 1191 (1901).

[23] R. G. Jones, *J. Amer. Chem. Soc.*, **69**, 2350 (1947).

[24] S. Swann, Jr., and W. E. Garrison, Jr., "Organic Syntheses," **41**, 33 (1961).

Table 3. The solvents of recrystallization, the analytical data, and the molecular-weights are recorded in Table 6, together with those of the reference substance.

The Rearrangement Reaction of IV_n. The reactions were carried out under an atmosphere of nitrogen. The procedure used for the synthesis of the cyclic tolan (V_{12}) will be described as a representative instance. A solution of the cyclic ethylene (IV_{12}, 507.9 mg, 1.12 mmol) in anhydrous ether (30 m*l*) was chilled in an ice-salt bath to keep at −17—−18°C. To the stirred solution we then added a solution of *n*-butyllithium (0.0561 mol/*l*, 22 m*l*, 1.23 mmol) over a period of 7 min. After stirring for a further hour at this tempearture, methanol (2 m*l*) and then water were added to the mixture. The organic layer was separated and dried. The colorless crystals (447 mg) obtained by evaporating the solvent were chromatographed on alumina (40 g). The fractions eluted with carbon tetrachloride gave the recovered ethylene (IV_{12}, 200 mg, 48.4%). The cyclic tolan (V_{12}, 200 mg, 46.8%) was obtained as colorless crystals from the fractions eluted with benzene. In the case of the reaction was performed at a temperature of −35°C, the cyclic tolan (V_{12}) was obtained in a yield of 46.4%, together with the recovered ethylene (53.4%)

The reaction conditions used for the preparation of the other cyclic tolans have already been described. The melting points, the yields, and the recovery of the ethylenes are tabulated in Table 7, together with those of the open-chain analogue. The cyclic tolans (V_n) were recrystallized from *n*-hexane.

Table 7. The analytical and the molecular-weight data of V_n and the reference substance

V_n		Analytical data (%) C	H	Mol wt
$n=11$	Found	82.64	8.31	432
	Calcd	82.83	8.34	363
12	Found	82.70	8.44	352
	Calcd	82.94	8.57	377
13	Found	82.79	8.82	398
	Calcd	83.03	8.77	391
14	Found	82.80	8.90	448
	Calcd	83.21	8.97	405
18	Found	83.40	9.60	496
	Calcd	83.43	9.63	460
n-Bu[a)]	Found	81.97	8.02	
	Calcd	81.95	8.13	

a) Recrystallized from ethyl acetate.

Attempted Synthesis of the Cyclic Tolan V_{10}. The cyclic ethylene (IV_{10}, 436 mg, 1.04 mmol) was treated with a 10% excess of *n*-butyllithium under the above-described reaction conditions. The reaction mixture turned greenish-yellow and then deep green. The deep green color faded to yellow on the addition of methanol (2 m*l*). The reaction mixture was then worked up, resulting in a greenish-yellow, resinous material. The sole substance which could be identified was the recovered ethylene (IV_{10}, 126 mg, 28.9%).