BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 177—184 (1971)

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

Mutsuo KATAOKA, Takashi ANDO, and Masazumi NAKAGAWA
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka

(Received July 13, 1970)

The polymethylene ether derivatives of *o,p'*-dihydroxydiphenylacetylene (VII_n, $n=7,8,9,10,11$ and 12) have been synthesized by the Fritsch-Buttenberg-Wiechell rearrangement. The electronic, infrared, and NMR spectra of VII_n were examined. It was observed that the increasing ring strain had a hypochromic effect, with a hypsochromic shift of the long-wavelength band in the electronic spectra of VI_n making a contrast with the bathochromic shift in the strained *p,p'*-bridged cyclic tolans.

The successful preparation of *p,p'*-bridged cyclic tolans by the Fritsch-Buttenberg-Wiechell rearrangement[2] prompted the present authors to the syntheses of *o,p'*-bridged cyclic tolans according to the same reaction. Just as in the case of the *p,p'*-series, the distance between the *o*- and the *p'*-positions of the two phenyl groups in the tolans is longer than that of in the 1,1-diarylethylenes; therefore, the rearrangement reaction may provide a route for the synthesis of strained *o,p'*-bridged cyclic tolans. The two benzene nuclei in the *p,p'*-series with a suitably-long bridging chain are forced to take a coplanar conformation. On the other hand, in the case of *o,p'*-bridged tolans, the spanning of the *o*- and *p'*-positions with a short bridging chain should result in a twisting of the two benzene rings. Therefore, the comparison of the electronic and the NMR spectroscopic behavior of the *o,p'*-bridged tolans with those of the *p,p'*-series seemed to be of interest.

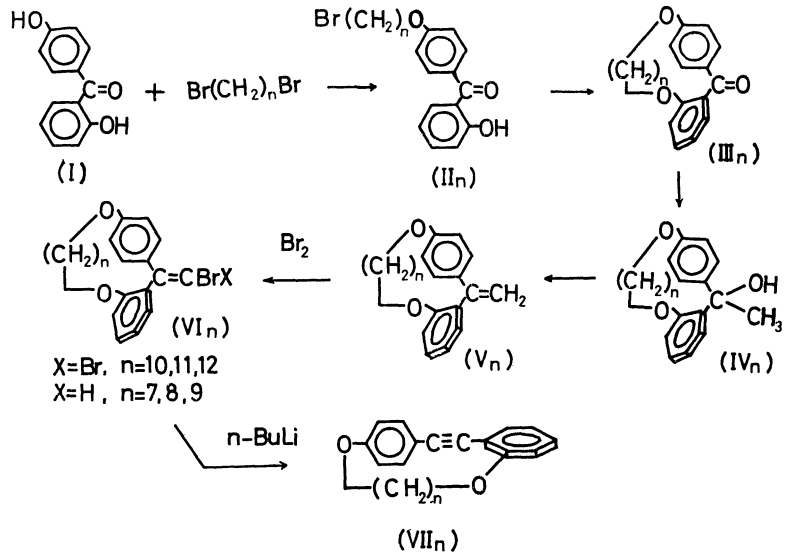
Synthesis. As is illustrated in Scheme 1, *o,p'*-dihydroxybenzophenone (I), which had been prepared by the intramolecular rearrangement of phenyl salicylate by stannic chloride,[3] was converted in a high yield to the *p'*-ω-bromopolymethylene ether derivative (II) by reaction with a large excess of polymethylene dibromide in the presence of equimolar potassium hydroxide.[4] Small amount of a diether derivative and the unreacted benzophenone (I) were also isolated. However, no *o*-alkylated compound could be obtained. This indicates the low reactivity of the *o*-hydroxyl group

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) Preceding paper.

3) W. Stadel, *Ann. Chem.*, **283**, 179 (1894).

4) *Cf.* A. Lüttringhaus and K. Ziegler, *ibid.*, **528**, 155 (1937); A. Lüttringhaus, *ibid.*, **528**, 211 (1937).



Scheme 1.

TABLE 1. THE REACTION CONDITIONS AND THE YIELDS OF III_n

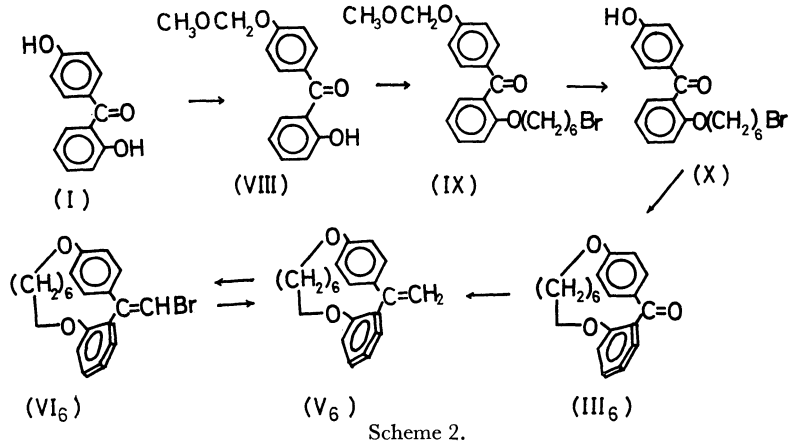
	II_n		III_n		
n	Amount (mmol)	Solvent (ml)	Reaction time (hr)	Yield (%)	Mp (°C)
12	22	600	35	45	94—96
11	26	600	66	85	99.0—99.7
10	24	600	30	50	not crystallized
9	35	600	77	65	163.7—164.8
8	42	1300	78	34	125.3—126.3
7	24	1000	66	13	102.3—103.6
6[a)]	12	1300	69	31	144.5—145.5

a) III_6 has been prepared according to a modified procedure.

hydrogen-bonded with the carbonyl oxygen. The intramolecular alkylation of II_n to yield the cyclic benzophenone derivative (III_n) was carried out in isoamyl alcohol in the presence of 3 equivalents of potassium carbonate under high-dilution conditions.[4] The reaction conditions and the yields of the intramolecular cyclization are summarized in Table 1, together with the melting points of the cyclic benzophenones (III_n). The low yields of III_{12} and III_{10} seemed to be due to the insufficient reaction period. On the other hand, the poor yields of III_8 and III_7 clearly indicate that the lengths of the bridging chains are unfavorable for the intramolecular alkylation. This suggests that the preparation of III_6 according to the above-mentioned procedure might not be feasible.

Consequently, the alternative procedure shown in Scheme 2 has been developed. The reaction of chloromethyl methyl ether with the monosodium salt of the dihydroxybenzophenone (I) in toluene afforded *o*-hydroxy-*p'*-methoxymethoxybenzophenone (VIII). The ω-bromohexyl ether (X) which was obtained by the reaction of hexamethylene dibromide with VIII according to the above-stated method, followed by an acid hydrolysis of the protective group, was subjected to intramolecular cyclization under high-dilution conditions to give the cyclic ether (III_6) in a reasonable yield.

The cyclic benzophenones (III_n and III_6) were converted to the corresponding methyl carbinols (IV_n and IV_6) by means of a large excess of methylmagnesium iodide. The 1,1-diarylethylenes (V_n and V_6) which were obtained by the acid dehydration of the carbinols were treated with bromine in carbon tetrachloride.[5] In the cases of n=12 and 11, the dibromides (VI_{12} and VI_{11}) were obtained in good yields. The bromina-



Scheme 2.

5) P. Pfeiffer and R. Wizinger, *Ann. Chem.*, **461**, 132 (1928).

tion of the decamethylene ether derivative (V_{10}) afforded the dibromide (VI_{10}, X=Br) contaminated with the monobromide (VI_{10}, X=H). The treatment of V_8 with 2 mole of bromine gave no crystalline product, and a prolonged reaction with an excess of bromine resulted in the formation of a product bearing a bromine atom in a phenyl group. Therefore, equimolar bromine was used to give a *cis-trans* mixture of the monobromide (VI_{9-6}) in the case of the lower homologue (V_{9-6}). The rearrangement reaction of VI_{12-6} was performed in ether employing 2 equivalents of *n*-butyllithium and at a temperature of −11——18°C. The yields and the melting points of the cyclic tolans (VII_n) are recorded in Table 2, together with those of an open-chain analogue, *o,p'*-dimethoxytolan.

Table 2. The yields and the melting points of the cyclic tolans (VII_n) and *o,p'*-dimethoxytolan

n	Yield (%)	Mp (°C)
7	22	121.7—122.7
8	42	137.0—137.6
9	56	127.6—128.0
10	73	143.8—144.4
11	75	101.4—102.0
12	63	120.0—120.6
CH_3O	17	68.0— 69.5

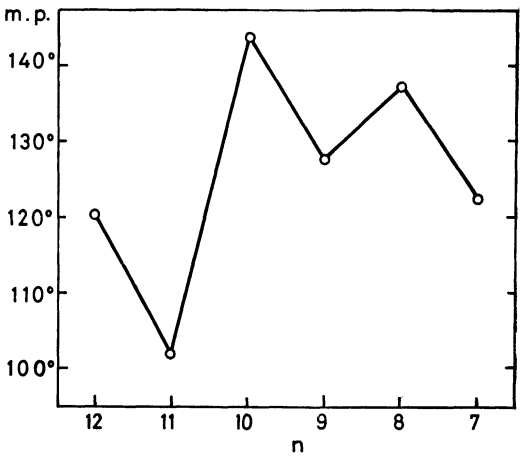


Fig. 1. The oscillation of the melting points of VII_n.

As is shown in Fig. 1, the cyclic tolans (VII_n) bearing an even number of methylene groups in the bridging chain exhibit higher melting points than the next higher or lower homologues having an odd number of methylene groups. This fact seems to indicate that the molecular geometry of VII_n is dependent not only on the length of the bridging chain, but also on whether the number of the methylene groups is odd or even.

In the case of VI_6, no cyclic tolan could be obtained, and the oily reaction product partly crystallized after standing overnight. The crystals were proved to be

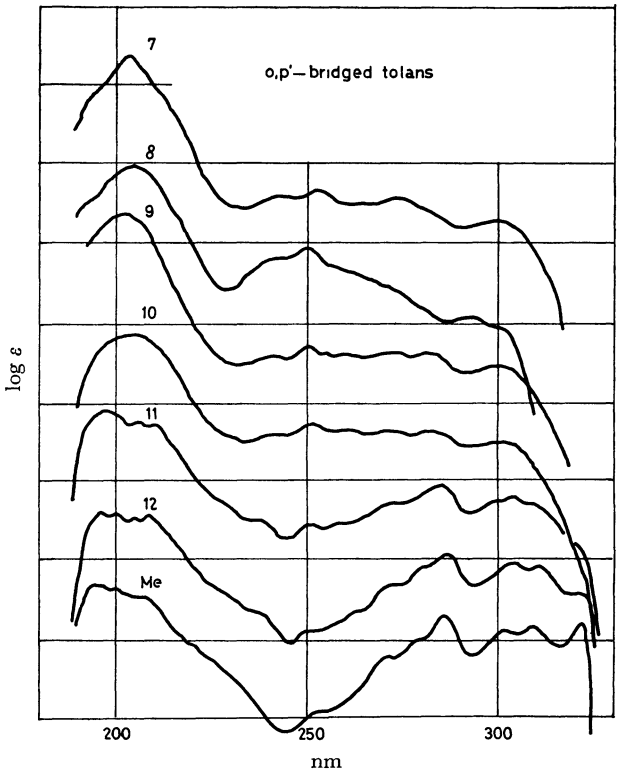


Fig. 2. The absorption curve of VII_n and *o,p'*-dimethoxytolan. The curves, with the exception of the dimethoxytolan at the bottom, have been displaced upward on the ordinate axis by 1/3 log ε unit increments from the curve immediately below, and the each horizontal lines correspond to log ε=4. (in *n*-hexane).

Table 3. The electronic spectral data of VII_n in *n*-hexane

n	λ_{max} in nm and $\varepsilon\times10^{-4}$ in parentheses												
12	197 (3.89)	201.5 (3.73)	206.5 (3.63)	210.5 (3.64)	238 (1.39)	252.5 (1.19)		272.5 (1.81)	289.5 (2.37)		305 (2.08)	311.5 (2.06)	324 (1.54)
11	195 (4.27)	201.5 (4.05)	206 (3.89)	210 (3.79)	239 (1.46)	252 (1.47)		275 (1.82)	285.5 (2.09)		304 (1.89)		
10			206 (4.46)		241 (1.63)	251.5 (1.83)	260 (1.67)	272.5 (1.66)	283 (1.64)		302 (1.51)		
9		202 (6.74)	208 (6.93)		241.5 (1.57)	252 (1.74)	262 (1.60)	274 (1.63)	283.5 (1.59)		302 (1.41)		
8			207 (5.44)		244* (1.99)	252 (2.15)				292 (1.09)	301 (1.02)		
7		204.5 (6.05)			243 (1.58)	253 (1.64)	263 (1.45)	274 (1.51)		298 (1.20)	302* (1.22)		
CH_3O	196 (3.62)							271 (1.78)	286.5 (2.56)		302.5 (2.26)	310.5 (2.30)	321.5 (2.33)

The asterisks indicate the shoulders.

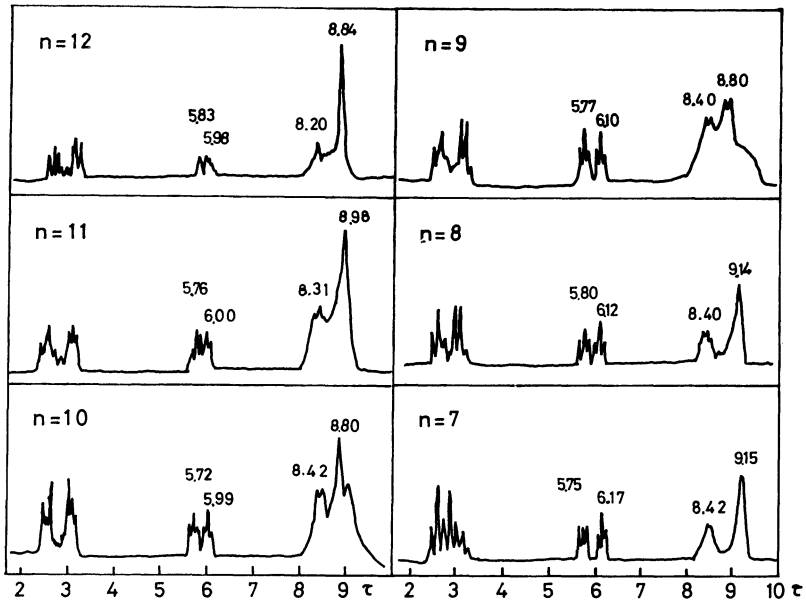


Fig. 3. The NMR spectra of VII_n.

the ethylene (V_6) on the basis of a mixed-melting-point determination and the thin-layer chromatographic, UV, IR, and NMR spectroscopic evidences. The structure of the oily product was not further studied. It is noteworthy that the yields of the cyclic tolans having a bridging chain of sufficient length are much higher than that of the open-chain analogue. As was pointed out previously,[1] the same trend has been observed in the case of the *p,p'*-series.

Electronic Spectra. The electronic spectral data of the cyclic tolans (VII_{12-7}), along with that of *o,p'*-dimethoxytolan as a reference, are recorded in Fig. 2 and Table 3. The reference substance exhibits a distinct, fine vibrational structure in the long-wavelength region. The gradual disappearanace of the fine structure according to the diminishing ring size is characteristic feature of the spectra of the cyclic tolans (VII_{12-7}).

Slight hypsochromic shifts of the absorption maxima at around 286 and 303 nm, accompanied by an appreciable hypochromic effect, were observed as the ring size decreased. On the other hand, the diminishing ring size exerted bathochromic and hyperchromic effects on the absorption peaks *ca.* 240 nm. The maximum ε-value of this peak was attained in the case of VI_{18}. The intensities of the peaks at *ca.* 250 nm gradually increased with the decrease in the number of *n*, and the maximum value was observed also in the case of VII_{18}.

The inspection of a molecular model of VII_7 indicates that the interplanar angle of the two benzene rings is almost rectangular. It is well-known that a twisted biphenyl derivative bearing bulky groups at the ortho positions exhibits an electronic spectrum resembling that of the ortho-substituted benzene moiety. However, no similarity was observed between the spectrum of VII_7 and that of *p*-methoxyphenylacetylene. This seems to indicate the presence of some conjugation of the two phenyl rings across the acetylenic linkage.

As the electronic spectra of the *o,p'*-bridged tolans (VII_n) suffer from the effects of both ring strain and the non-coplanarity of the two benzene nuclei, it is difficult to deduce the effect of strain from the above-mentioned spectral behavior. However, it seems to be pertinent to conclude that the increasing strain has hypsochromic and hypochromic effects on the long-wavelength band in the spectra of VII_n. The same tendency has been observed in the case of *o,o'*-bridged diphenyldiacetylenes.[6]

Nuclear Magnetic Resonance Spectra. The NMR spectra of the cyclic tolans (VII_n) are recorded in Fig. 3. The multiplets at around 2—3 τ can be assigned to the aromatic protons. Intense peaks, consisting of two poorly-resolved portions were observed at 8.0—9.7 τ in the spectra of VII_{12-9}. In the cases of VII_8 and VII_7, the peaks split into two peaks *ca.* 8.4 τ and *ca.* 9.15 τ. The higher-field peak can be assigned to the protons of methylene chain, except the α- and β-methylenes to the oxygen atoms. The peaks at 8.40 τ and 8.42 τ in VII_8 and VII_7 and the lower-field peaks in the poorly-resolved signals in VII_{12-9} were assigned to the protons of β-methylene to the oxygen atoms, considering the results of the assignment in *p,p'*-bridged tolans.[2] The two triplets observed around 6 τ were assigned to the methylene protons adjacent to the ortho- and para-oxygen atoms. The change in the chain length should alter the conformation of the tolan system as well as the relative configuration of $-O-CH_2-$ with respect to the planes of the benzene rings, resulting in a change in the shielding or deshielding effects of the benzene or the acetylene, and also in a change of the electron density on the oxygen atoms. This complicated situation makes it difficult to discriminate between the α-methylene attached to the para-oxygen and that linked with the ortho-oxygen. The above-mentioned assignments are summarized in Table 4, along with that of *o,p'*-dimethoxytolan.

6) F. Toda and M. Nakagawa, This Bulletin, **34**, 862 (1961).

The rather sharp peak at 8.84 τ in the poorly-resolved broad signal of VII_{12} seems to reflect the conformational mobility of the long bridging chain. The broadening of the corresponding signals in VII_{11-9} with the decrease in the number of n is attributable to some restriction of the conformational mobility of the bridging chain of a medium length. Consequently, the splitting of the two portions of the signals which was observed in the spectra of VII_8 and VII_7 seems to indicate a rigid structure in the cyclic tolans bearing short bridging chains.

Table 4. The assignment of the NMR spectra of VII_n (60 MHz in CCl_4, τ-value)

VII_n	Aromatic	α-Methylene		β-Methylene	Other methylene
12	2—3	5.98(2H)	5.83(2H)	8.20	8.84(20H)
11	2—3	6.00(2H)	5.76(2H)	8.31	8.98(18H)
10	2—3	5.99(2H)	5.72(2H)	8.42	8.80(16H)
9	2—3	6.10(2H)	5.77(2H)	8.40	8.80(14H)
8	2—3	6.12(2H)	5.80(2H)	8.40(4H)	9.14(8H)
7	2—3	6.17(2H)	5.75(2H)	8.42(4H)	9.15(6H)
CH_3O	2—3	6.06(3H)	5.77(3H)		

Infrared Spectra. It was observed that the cyclic tolans bearing a bridging chain with an odd number of methylene groups exhibit sharper IR spectra than those of the even-number homologues. This fact seems to have some correlation with the above-mentioned oscillation of the melting points (Fig. 1). The characteristic peaks in the IR spectra of VII_n are summarized in Table 5, along with the spectrum of *o,p'*-dimethoxytolan.

Table 5. The IR spectra of VII_n (KBr-disk)

VII_n	$\nu_{C\equiv C}$	$\nu_{C=C}$ (arom.)	δ_{CH} (arom.)	
12	2215 (w)	1605 (s) 1571 (w)	825 (s)	744 (s) cm^{-1}
11	2210 (w)	1604 (s) 1569 (m)	839 (s)	745 (s)
10	2220 (w)	1607 (s) 1570 (m)	829 (s)	750 (s)
9	2210 (w)	1603 (s) 1570 (w)	835 (s)	748 (s)
8	2210 (w)	1604 (s) 1573 (m)	836 (s)	749 (s)
7	2200 (w)	1602 (s) 1570 (w)	841 (s)	748 (s)
CH_3O	2220 (w)	1609 (s) 1574 (m)	830 (s)	749 (s)

Experimental

All the melting points are uncorrected. The electronic spectra were measured on a Hitachi EPS-2 Spectrophotometer; the infrared spectra, with a Hitachi EPI-2 Spectrophotometer, and the NMR spectra, with a Varian A 60 Spectrometer. The molecular weights were determined by the Rast method.

1,12-Dibromododecane and 1,11-Dibromoundecane. The polymethylene dibromides were prepared according to the method described in the preceding paper.[2]

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

1,9-Dibromononane. Dimethyl 1,9-nonanedioate which had been prepared from azelaic acid[7] was reduced by means of lithium aluminum hydride; this yielded 1,9-nonanediol. The treatment of the diol (62.8 g, 0.39 mol) with hydrogen bromide (30% excess) at 130°C[8] afforded 1,9-dibromononane; bp 120—126°C/4 mmHg, 86.1 g (72%).

1,8-Dibromooctane. The Hunsdiecker reaction of silver sebacate[9] gave the dibromide in a yield of 40%.

1,7-Dibromoheptane. Silver 1,9-nonanedioate (200 g, 0.5 mol) in dry carbon tetrachloride was treated with bromine (56 m*l*, 1.1 mol) to yield the dibromide (61 g, 47%).[10]

1,6-Dibromohexane. To a stirred solution of lithium aluminum hydride (45 g, 1.2 mol) in dry ether (1 *l*), there was added a solution of dimethyl adipate (159 g, 0.92 mol) in ether (700 m*l*) at such a rate that the ether refluxed gently (100 min were required). After refluxing for 3 more hr, ethyl acetate (50 m*l*) was added to the cooled reaction mixture, and then 20% sulfuric acid (1.5 *l*) was added under ice-cooling. After the removal of the ether by distillation, the water was evaporated under reduced pressure. The crystalline solid obtained was dried *in vacuo* at 100°C for 8 hr. Ethanol (400 m*l*) was mixed the solid, and the mixture was refluxed for 4 hr. The ethanol was then separated by decantation. This procedure was repeated 6 times. The combined ethanol extracts were evaporated under reduced pressure. The residue was redissolved in anhydrous ethanol, and the insoluble material was removed by filtration. After the removal of the solvent from the filtrate *in vacuo*, the residue was distilled *in vacuo* to afford 1,6-hexanediol (bp 115—124°C/4—7 mmHg, mp 40—42°C, 68 g, 63%). The diol (79 g, 0.67 mol) was converted to 1,6-dibromohexane (bp 128—133°C/23—25 mmHg, 106 g, 65%) according to a previously described method.[8]

Preparation of o-Hydroxy-p'-ω-bromoalkyloxybenzophenones (II_n). As all the syntheses of *p'*-ω-bromopolymethylene ethers (II_n) were carried out under almost the same reaction conditions, the procedure used in the preparation of *p'*-10-bromodecyl ether (II_{10}) will be described as a representative example. To a stirred and refluxing solution of 1,10-dibromodecane (105 g, 0.35 mol) and *o,p'*-dihydroxybenzophenone (10 g, 47 mmol) in anhydrous ethanol (150 m*l*), there was added a solution of potassium hydroxide in ethanol (1.08N, 43.3 m*l*, 47 mmol) over a period of 1 hr. The reaction mixture immediately turned red, and then there was a deposition of fine crystals of potassium bromide. After the addition had been completed, refluxing was continued for a further 40 min. During this period, the reaction mixture turned yellowish brown and the pH-value of the mixture showed 5.5. The residue obtained by evaporating the solvent under reduced pressure was mixed with water (300 m*l*) and extracted with ether. The extract was then worked up according to the usual manner, and the excess of the dibromide was recovered by distillation (bp 138—141°C/5 mmHg). The yellow oily residue (15.2 g) in benzene was chromatographed on alumina (40 g). The fractions eluted with benzene afforded II_{10} (10.2 g, 68%) as a yellow liquid. Small amounts of the diether derivative and unreacted benzophenone (I) were obtained. These compounds could be easily discriminated by the difference in $\nu_{C=O}$ and ν_{O-H} as is shown in Table 6. The monoethers (II_n) were obtained as yellow liquid, except in the case of $n=12$, which gave yellow crystals in a yield of 46%. The yields of the other members were found to be

7) *Cf.* L. J. Durham, D. J. McLeod, and J. Cason, "Organic Syntheses," Coll. Vol. IV, p. 635 (1963).
8) *Cf.* W. L. McEwen, *ibid.*, Coll. Vol. III. p. 227 (1955).
9) F. L. M. Pattison, *J. Org. Chem.*, **21**, 745 (1956).
10) *Cf.* C. V. Wilson, "Organic Reactions," Vol. 9, ed. by R. Adams, John Wiley and Sons, New York, N. Y. (1957), p. 332.

TABLE 6. THE $\nu_{C=O}$ AND ν_{O-H} OF THE ETHERS AND I (cm^{-1})

	o,p'-Diether	*p'*-Ether (II_n)	*o*-Ether[a] (II_6)	I
$\nu_{C=O}$	1660	1630	1650	1630
ν_{O-H}	—	2900	3200	3250

a) This compound was prepared by a modified method. See below.

as follows: II_{11}: quantitative; II_{10}: 68%; II_9: 74%; II_8: 57% and II_6: 63%. The monoethers (II_n) thus obtained were subjected to the subsequent reaction without further purification.

Syntheses of the Cyclic Ethers (III_n). As the reaction conditions of the intramolecular cyclization of II_n and the yields of III_n have been shown in Table 1, the method of the synthesis of III_8 will be described as an example. The ω-bromoether (II_8, 17.1 g, 42 mmol) in isoamyl alcohol (310 m*l*) was added slowly to a vigorously-stirred and refluxing mixture of potassium carbonate (17.5 g, 0.13 mol) and isoamyl alcohol (960 m*l*) over a period of 74 hr, employing a high-dilution apparatus.[4] After the addition had been completed, the the reaction mixture was refluxed for a further 4 hr under stirring. The inorganic material was then removed by filtration. The resinous material obtained by evaporating the solvent under reduced pressure was dissolved in benzene and chromatographed on alumina (300 g). The fractions eluted with benzene - ether (1 : 1) gave III_8 (4.66 g, 34%) as colorless crystals. This substance was recrystallized twice from *n*-hexane - methanol to yield pure III_8 as colorless plates: mp 125.3—126.3°C. The analytical data, the molecular weights, and the solvents of the recrystallization of III_n are recorded in Table 7. The crude crystals of III_{12} and the liquid III_{10} were used for the following reaction without further purification.

TABLE 7. THE ANALYTICAL DATA, THE MOLECULAR WEIGHT, AND THE SOLVENTS OF RECRYSTALLIZATION OF III_n

III_n		Analytical data (%) C	H	Mol wt	Solvent
11	Found	78.93	8.26	358	H
	Calcd	78.65	8.25	366	
9	Found	77.84	7.69		H-B
	Calcd	78.07	7.74		
8	Found	77.63	7.50	318	H-B
	Calcd	77.75	7.46	324	
7	Found	77.76	7.18	314	H
	Calcd	77.39	7.14	310	
6[a]	Found	76.96	6.73	302	H-B
	Calcd	77.00	6.80	296	

a) This was prepared by a modified method. See below.
H=*n*-hexane; B=benzene

o-Hydroxy-p'-methoxymethoxybenzophenone (VIII). A solution of sodium ethoxide in ethanol, prepared from sodium (1.76 g, 73 mg atom) and ethanol (50 m*l*), was added to a solution of the dihydroxybenzophenone (I, 15.5 g, 73 mmol) in ethanol (150 m*l*). The mixture turned red, and the precipitation of a yellow solid was observed. The solvent was then removed under reduced pressure, and toluene (200 m*l*) was added to the residue. The toluene was subsequently evaporated again under reduced pressure. The procedure was repeated to remove the traces of ethanol and water. The sodium salt obtained as a yellow powder was mixed with toluene (200 m*l*), and then chloromethyl methyl ether (5.85 g, 73 mmol) was added dropwise under stirring. After having been stirred overnight, the reaction mixture was washed successively with a 10% sodium hydrogen carbonate solution, water, and a saturated sodium chloride solution, and then dried. The oily material (17.2 g) obtained by evaporating the solvent was chromatographed on alumina (190 g). The fractions eluted with benzene - ether (1 : 1), ether, and ether containing 3% of methanol, gave VIII (12.0 g 64%) as a liquid, IR (neat): ν_{O-H} 2900; $\nu_{C=O}$ 1630 cm^{-1}.

o-ω-Bromo-n-hexyloxy-p'-methoxymethoxybenzophenone (IX). Thirty-one m*l* of 1.03N solution of potassium hydroxide in ethanol was added, over a period of 1 hr, to a stirred and refluxing solution of VIII (7.99 g, 31 mmol) and 1,6-dibromohexane (105 g, 0.43 mol) in anhydrous ethanol (150 m*l*). After refluxing for further 1.5 hr, the solvent was removed under reduced pressure. Benzene was added to the residue, and it was washed with a 10% sodium hydroxide solution. The benzene solution was worked up in the usual manner, and the dibromohexane was removed by vaccum distillation; this yielded IX as a yellow liquid (5.63 g, 42%). IR (neat): ν_{O-H} absent; $\nu_{C=O}$ 1660 cm^{-1}. The aqueous layer was neutralized by dilute hydrochloric acid and extracted with benzene. The structure of *o-ω*-bromohexyloxy-*p'*-hydroxybenzophenone (X) was assigned to the oily substance obtained from the benzene layer on the basis of its IR spectrum (ν_{O-H} 3200; $\nu_{C=O}$ 1650 cm^{-1}). The prolonged reaction (7.5 hr) of VIII (11.5 g, 43 mmol) with the dibromohexane (73 g, 0.30 mol) in the presence of 64.5 mmol of potassium hydroxide resulted in the formation of *o,p'*-bis-ω-bromohexyloxybenzophenone (10.2 g, 47%) and *o-ω*-bromohexyloxy-*p'*-hydroxybenzophenone (X, 9.40 g, 58%). The cleavage of the acetal linkage in an alkaline medium seemed to be noteworthy.

o-ω-Bromo-n-hexyloxy-p'-hydroxybenzophenone (X). A mixture of IX (4.51 g, 12 mmol), acetic acid (25 m*l*), water (25 m*l*), and concentrated sulfuric acid (0.2 g) was refluxed for 15 min under stirring. The reaction mixture was then worked up according to the usual manner to afford crude X (4.80 g, 95%, IR (neat): ν_{O-H} 3200; $\nu_{C=O}$ 1650 cm^{-1}). This was subjected to the subsequent reaction without any further purification.

o,p'-Dihydroxybenzophenone Hexamethylene Ether (III_6). The intramolecular alkylation under high-dilution conditions described in the preparation of III_n was successfully adapted in this case. The product (4.50 g) obtained from X (4.51 g, 12 mmol) was chromatographed on alumina (135 g). The fractions eluted with benzene - ether (9 : 1～2 : 1) afforded, upon work-up, 1.08 g (31%) of III_6 as colorless crystals. This substance was recrystallized from *n*-hexane - benzene to give pure III_6 (for analytical data, see Table 7).

o,p'-Dimethoxybenzophenone. To a stirred and refluxing mixture of the dihydroxybenzophenone (I, 3.0 g, 14 mmol), methyl iodide (5 m*l*, 80 mmol), and anhydrous ethanol (25 m*l*), we added 28 m*l* of a 1N solution of potassium hydroxide in ethanol over a period of 70 min; refluxing was then continued for 1 hr. The presence of the hydroxyl group was revealed by the IR spectrum of the crude product. Therefore, the crude product was treated in the same way, and dimethoxybenzophenone (3.02 g, 89%) was afforded as a liquid.

o,p'-Di-n-butoxybenzophenone. According to the procedure described above, the reaction of the dihydroxybenzophenone with *n*-butyl bromide gave the dibutoxybenzophenone as a liquid in a yield of 74%.

Syntheses of the Methyl Carbinols (IV_n). The preparation of the methyl carbinol (IV_8) will be described as a re-

presentative example. To a stirred and ice-cooled solution of methylmagnesium iodide, prepared from magnesium (0.5g 0.021 g atom), methyl iodide (21 m*l*, 32 mmol) and ether (20 m*l*), we added, drop by drop a solution of III_8 (1.18 g, 5.6 mmol) in anhydrous benzene (30 m*l*). The mixture was refluxed for 2 hr; then a 10% aqueous solution of ammonium chloride was added to the ice-cooled reaction mixture. The benzene layer was then worked up to yield colorless crystals (1.80 g, 95%). This substance was recrystallized 4 times from *n*-hexane to yield pure IV_8; mp 84.0—86.0°C, colorless needles. The yields of the methyl carbinols were found to be as follows: IV_6: quantitative, IV_7*: 99%, IV_8: 95%, IV_9*: 85%, IV_{10}: quantitative, IV_{11}*: 87%, IV_{12}*: 90%, dimethoxy derivative: 94%, dibutoxy derivative*: 86%. The carbinols denoted by asterisks were obtained as liquids and could not be crystallized. The melting points, the analytical data, and the solvents of recrystallization are summarized in Table 8.

Table 8. The melting points, the analytical data, and the solvents of recrystallization of IV_n and the reference substance

IV_n	Mp (°C)		Analytical data (%) C	H	Solvent
10	76.3—77.0	Found	78.44	8.83	H
		Cacld	78.22	8.75	
8	84.0—86.0	Found	77.83	8.43	H
		Calcd	77.61	8.29	
6	143.0—143.9	Found	76.82	7.73	B-H
		Calcd	76.89	7.74	
CH_3O	99—103[a]				

a) Slightly impure material. H=*n*-hexane; B=benzene.

1-(o-Hydroxyphenyl)-1-(p'-hydroxyphenyl)ethylene Polymethylene Ethers (V_n). The Dehydration of the Methyl Carbinols (IV_n). The preparation of V_8 will be described as an example. A mixture of IV_8 (1.82 g, 54 mmol) and 8N sulfuric acid (60 m*l*) was refluxed for 1 hr under stirring, and then it was extracted with benzene. The extract afforded, upon work-up, 1.58 g (91%) of colorless crystals. This substance was recrystallized 3 times from *n*-hexane - methanol to give pure V_8, mp 80.0—81.0°C as colorless plates.

According to the same procedure, all the carbinols (IV_n) gave the ethylenes (V_n) in yields over 90%. The pure ethylenes (V_6, V_8 and V_{11}) were obtained by recrystallizing the crude materials from *n*-hexane - methanol (1 : 1). The melting points, the analytical data of V_n, and the reference substance are given in Table 9.

Table 9. The melting points and the analytical data of V_n and the reference compounds

V_n	Mp (°C)		Analytical data (%) C	H
6	126.0—126.7	Found	81.71	7.51
		Calcd	81.60	7.53
7	113—115[a]			
8	80.0—81.0	Found	81.73	8.13
		Calcd	81.95	8.13
9	crystalline solid[a]			
10	liquid[a]			
11	99.0—100.5	Found	82.38	8.86
		Calcd	82.37	8.85
CH_3O	75—77[a]			
n-BuO	liquid[a]			

a) The ethylenes denoted by asterisks were used for the subsequent reaction without further purification.

1-(o-Hydroxyphenyl)-1-(p'-hydroxyphenyl)-2,2-dibromoethylenes (VI_n, n=10, 11, 12, X=Br). The preparation of VI_{12} will be described as a representative instance. To a solution of V_{12} (2.36 g, 6.2 mmol) in carbon tetrachloride (30 m*l*), there was added a solution of bromine in the same solvent (0.63 mol/*l*, 19.8 m*l*, 13 mmol). The mixture was stirred for 1 hr under reflux, resulting in the disappearance of the color of the bromine. The same amount of the bromine solution was added to the reaction mixture, and the new mixture refluxed for 2 more hr. The residue obtained by evaporating the solvent under reduced pressure was mixed with benzene (50 m*l*). The benzene solution was washed successively with a 10% sodium hydroxide solution and water, and then dried. The evaporation of the solvent gave 2.96 g of an oily material. This was chromatographed on alumina (40 g) to afford yellowish crystals; 2.49 g (75%). The crystals were recrystallized 3 times from ethyl acetate - methanol to yield pure VI_{12} as colorless leaflets; mp 99.7—101.5°C.

The melting points, the analytical data, and the molecular weights of V_{10-12} and the reference substances are shown in Table 10, together with the solvents used for the recrystallization.

Table 10. The melting points, the analytical data, and the molecular weights of VI_{10-12} and the reference compounds

VI_n	Mp (°C)		Analytical data (%) C	H	Cl	Mol wt	Solvent
12	99.7—	Found	58.08	5.98	29.61	518	E-M
	101.5	Calcd	58.22	6.01	29.80	504	
11	103.6—	Found	58.07	5.87	29.52		H
	104.6	Calcd	57.48	5.79	30.60		
10	92.4—	Found	57.04	5.79	31.20	345	H
	94.6	Calcd	56.71	5.55	31.44	348	
CH_3O	93.5—	Found	48.47	3.56	40.83		E-M
	94.6	Calcd	28.27	3.54	40.15		
n-BuO	72.7—	Found	54.75	5.43	33.63		E-M
	73.4	Calcd	54.79	5.43	33.14		

E=ethyl acetate; M=methanol; H=*n*-hexane.

cis- and trans-1-(o-Hydroxyphenyl)-1-(p'-hydroxyphenyl)-2-bromoethylene Polymethylene Ethers (VI_n, n=9, 8, 7, 6, X=H). The procedure used for the preparation of VI_9 will be described as an example. A solution of V_9 (862 mg, 2.6 mmol) in carbon tetrachloride (40 m*l*) was mixed with a solution of bromine in the same solvent (0.249 mol/*l*, 10.3 m*l*, 26 mmol). After refluxing for 1 hr, the solvent was distilled out under reduced pressure. The residue in *n*-hexane - benzene was passed through a short column of alumina. The oily material obtained by evaporating the solvent *in vacuo* crystallized on standing overnight in a refrigerator. The crude crystals were chromatographed twice on alumina (30 g) to yield 600 mg (56%) of VI_9. An analytical specimen (colorless plates, mp 88—101°C) was obtained by recrystallizing the crystals 4 times from *n*-hexane.

Found: C, 66.99; H, 6.62; Br, 18.94%. Mol wt: 286. Calcd for $C_{23}H_{27}O_2Br$: C, 66.50; H, 6.55; Br, 19.24%. Mol wt: 415.

As the bromoethylenes (VI_8, VI_7, and VI_6) were obtained

as oily materials and could not be crystallized, the bromoethylenes purified by chromatography on alumina were subjected to the following reaction.

Formation of the Cyclic Tolans (VIII$_n$, n=12, 11, 10, 9, 8 and 7). The procedure of the rearrangement to form the cyclic tolan is exemplified by the case of $n=12$. To a solution of VI$_{12}$ (680 mg, 1.3 mmol) in anhydrous ether (30 ml) which had been cooled in an ice-salt-bath, there was added, drop by drop a solution of *n*-butyllithium in ether (0.15 mol/l, 17 ml, 2.6 mmol) under stirring. A rise of temperature from −16°C to −11°C was observed on the addition of the reagent. Stirring was continued for one more hr at a temperature of −16——17°C. The reaction mixture was then washed with water, and the aqueous layer was extracted with benzene. The extract was combined with the organic layer and was worked up in the usual manner to yield colorless crystals (460 mg, 96%). The crude crystals were recrystallized twice from *n*-hexane to afford 300 mg (63%) of pure VII$_{12}$, mp 120.0—120.6°C as colorless cubes.

In the cases of $n=8$ and 7, the crude crystals were subjected to chromatography on alumina 3 times, and the oily by-product could be removed by elution with petroleum benzine - benzene (1 : 1). The pure VII$_8$ and VII$_7$ were obtained from the fractions eluted with ether. Also, the reference substance, *o,p'*-dimethoxytolan, was obtained as liquid; crystallization was achieved after repeating the chromatography on alumina.

The analytical data, the molecular weights, and the solvents of the recrystallization of VII$_n$ are summarized in Table 11 (for the yields and the melting points of VII$_n$, see Table 2).

Attempted Synthesis of VII$_6$. The treatment of VI$_6$ (323 mg, 0.87 mmol) with *n*-butyllithium according to the above-mentioned procedure afforded a yellow, oily product (291 mg) which partly crystallized on standing overnight. The product gave a negative Beilstein test. Thin-layer chromatography of the reaction product 3 gave spots, R_f 6.1 (brown), R_f 5.5 (red), R_f 4.9 (purple), and R_f 1.5 (blue) (adsorbent: alumina; solvent: benzine - benzene (4 : 1); detection reagent: conc. sulfuric acid). It was found that the constituents which gave the spots at R_f 5.5 and 4.9 were the main products. The product which gave the spot at R_f 4.9 could be isolated as crystals by chromatography on alumina. This substance was proved to be identical with the cyclic ethylene (V$_6$) on the basis of the IR and NMR spectroscopic evidence and a mixed-melting-point determinaion. Another product (R_f 5.5), obtained as an oil, has not yet been chracterised.

TABLE 11. THE ANALYTICAL DATA, THE MOLECULAR WEIGHTS, AND THE SOLVENTS OF RECRYSTALLIZATION OF VII$_n$ AND THE REFERENCE COMPOUND

VII$_n$		Analytical data (%) C	H	Mol wt	Solvent
12	Found	83.09	8.59	368	H
	Calcd	82.93	8.57	378	
11	Found	82.52	8.26	352	H
	Calcd	82.83	8.34	362	
10	Found	82.82	8.09	345	B-H
	Calcd	82.72	8.10	348	
9	Found	82.44	7.82	325	H
	Calcd	82.59	7.84	334	
8	Found	82.55	7.60	334	H
	Calcd	82.46	7.55	320	
7	Found	82.12	7.28	288	H
	Calcd	82.32	7.24	306	
CH_3O	Found	80.58	5.92		H
	Calcd	80.64	5.92		

H=*n*-hexane; B=benzene