Oligomers and Polymers Containing Triple Bonds. III. Derivatives of α,ω-Bis(4-ethynylphenoxy)alkane[1]

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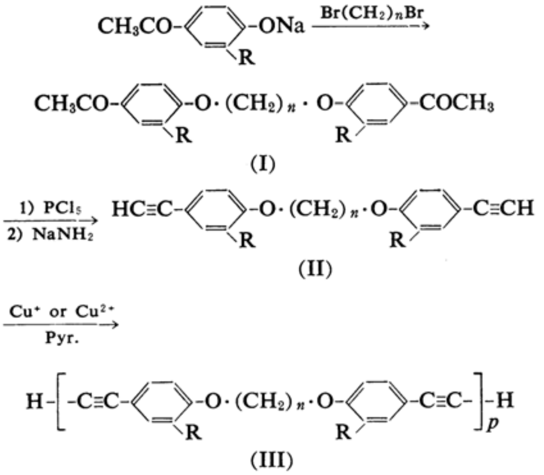
In previous papers[2,3] the oxidative polymerization of conjugated diethynyl compounds to produce conjugated linear polymers containing triple bonds has been reported.

The present paper deals with the oxidative polymerization of non-conjugated diethynyl compounds, α, ω-bis(4-ethynylphenoxy)alkanes (II: R=H) and α,ω-bis(4-ethynyl-2-methylphenoxy)alkanes (II: $R=CH_3$). In connection with the polymerization, the relation among the kinds of catalysts, the degree of polymerization and the crystallinity of polymers and that between the degree of polymerization and the length of the polymethylenic chain of the monomeric compound (*n*) have been studied.



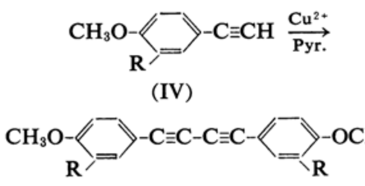
(I)

(II)

(III)

$R=H$: $n=1,2,3,4,5,6$ and 10

$R=CH_3$: $n=1,2,3,4,5$ and 6



(IV)

(V) $R=H, CH_3$

The influence of a methyl group substituted at the benzene ring on the degree of polymerization and on the crystallinity has also been investigated.

Following the method employed for the preparation of α, ω-di(2-ethynylphenoxy)alkane,[4] sodium 4-acetylphenoxide or sodium 4-acetyl-2-methylphenoxide was treated with α, ω-dibromoalkanes in boiling dimethylformamide to produce the diketones (I: R=H or $R=CH_3$), usually in moderate yields. These diketones were then converted to the chlorinated compounds with phosphorus pentachloride, followed by dehydrochlorination with sodium amide in liquid ammonia to give the diethynyl compounds (II).

The oxidative polymerization of the diethynyl monomers (II) using cupric or cuprous salt in pyridine afforded the corresponding polymers, which were insoluble in common organic solvents. Under some conditions, however, some linear oligomers were produced; for example, when the polymerization of a monomer (II: $R=CH_3$, $n=6$) was carried out using cupric salt in pyridine-methanol, the linear dimer (III: $R=CH_3$, $n=6$) was obtained as colorless crystals. Although the polymers were stable at temperatures below 150°C, when heated above 200°C in a air bath they turned brown and finally black.

The infrared spectra of most of the polymers show the ethynyl absorption band at ca. 3300 cm^{-1} (Fig. 1); this provides evidence for the linear structure of the polymers. Another confirmatory piece of evidence for the structure involving diphenyldiacetylene and diphenoxyalkane linkages was obtained by comparing the infrared spectra of the polymers with those of standard compounds involving the monomers II, the linear dimer (II: $R=CH_3$, $n=6$, $p=2$), 4, 4′-dimethoxydiphenyldiacetylene (V: R=H) and 4, 4′-dimethoxy-3, 3′-dimethyldiphenyldiacetylene (V: $R=CH_3$).

The degree of polymerization of the polymer (III) was estimated by comparing the intensity of the ethynyl absorption maximum with that of the corresponding monomer (II),[1,2] as represented by the example shown in Fig. 1.

Although some polymers (III: $R=CH_3$, $n=$ 1, 3, 5) do not show any ethynyl band at ca.

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[1] Preliminary report: *Chem. & Ind.*, **1962**, 1980.

[2] H. Tani, F. Toda and K. Matsumiya, This Bulletin, **36**, 391 (1963).

[3] H. Tani, S. Tanaka and F. Toda, ibid., **36**, 1268 (1963).

[4] F. Toda and M. Nakagawa, ibid., **34**, 862 (1961).

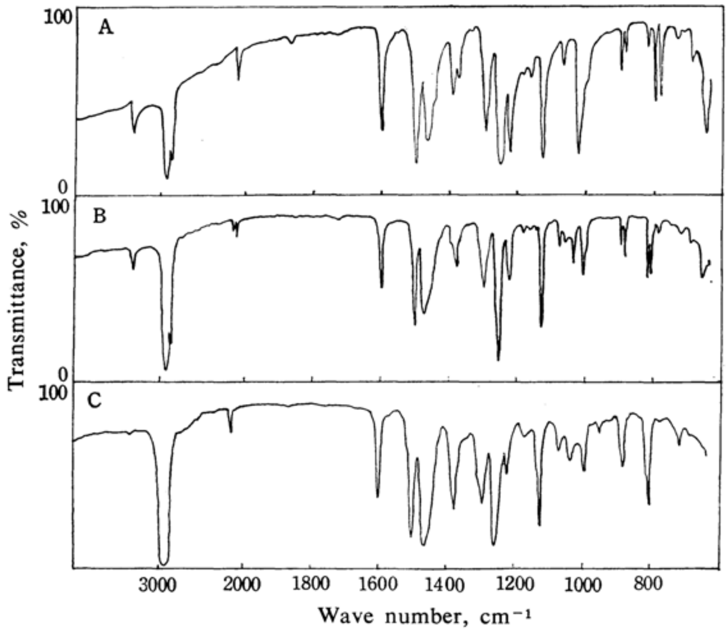

Fig. 1. Infrared spectra (Nujol mull).

A: α,ω-Bis(4-ethynyl-2-methylphenoxy)hexane (II: $R=CH_3$, $n=6$)
B: Linear dimer of II $R=CH_3$, $n=6$ (III: $R=CH_3$, $n=6$, $p=2$)
C: Polymer (III: $R=CH_3$, $n=6$, $p=36$)

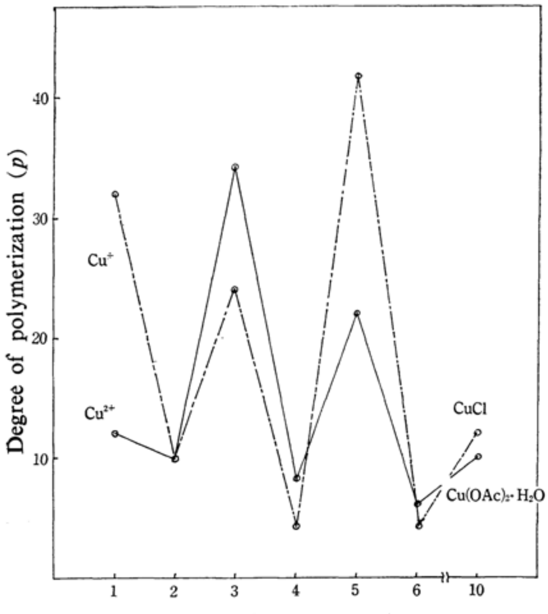

Fig. 2. Relation between the degree of polymerization (p) and the number of methylene (n) in the oxidative polymerization of II: $R=H$.

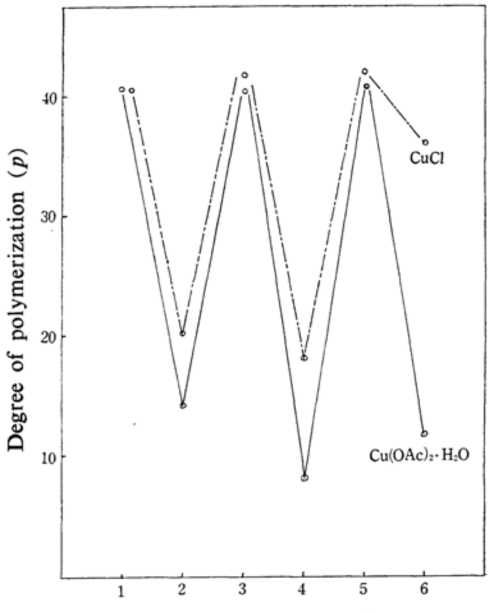

Fig. 3. Relation between the degree of polymerization (p) and the number of methylene (n) in the oxidative polymerization of II: $R=CH_3$.

TABLE I. OXIDATIVE POLYMERIZATION OF α,ω-BIS(4-ETHYNYLPHENOXY)ALKANE (II: R=H)

II: R=H		Catalyst			Reaction		Atmosphere	Degree of polymerization
n	mg.	CuCl mg.	$Cu(OAc)_2\cdot H_2O$ mg.	Pyridine ml.	Temp. °C	Time min.		p
1	200		800	15	55	70	Air	12
	300	300		50	55	70	Air	32
2	50		500	10	60	150	Air	10
	50	50		10	50	75	O_2	10
3	300		2800	25	60	95	Air	34
	200	200		15	45	80	O_2	24
4	70		300	15	55	70	Air	8
	70	50		15	60	120	O_2	4
5	100		400	10	55	100	Air	22
	100	100		10	55	100	Air	42
6	100		400	20	50	110	Air	6
	100	100		20	55	120	O_2	4
10	100		400	20	55	100	Air	10
	100	100		20	55	100	Air	12

TABLE II. OXIDATIVE POLYMERIZATION OF α,ω-BIS(4-ETHYNYL-2-METHYLPHENOXY)ALKANE (II: $R=CH_3$)

All reactions were carried out at 55°C under atmosphere of air.

II: $R=CH_3$		Catalyst			Reaction time	Degree of polymerization
n	mg.	CuCl mg.	$Cu(OAc)_2\cdot H_2O$ mg.	Pyridine ml.	min.	p
1	100		400	15	60	>36
	100	100		15	60	>36
2	60		240	10	90	14
	60	60		10	90	20
3	100		400	10	100	>36
	100	100		10	100	>36
4	100		400	10	100	8
	100	100		10	100	18
5	40		160	6	100	>36
	40	40		10	100	>36
6	100		400	10	100	12
	100	100		10	100	36

3300 cm^{-}, their degrees of polymerization are assumed to be higher than 36, since the monomer (II: R=H, n=1, 3 and 5) with an odd number of n yielded higher polymers than those obtained from the monomers (II: R=H, n=2, 4, 6 and 10) showing even mumbers of n, as is shown in Figs. 2 and 3 as well as in Tables I and II, moreover, the polymer (III: $R=CH_3$, n=4) was estimated to have 36 degree of polymerization according to the spectral estimation cited above.

The high crystallinity of the polymers (III) shown by the X-ray diagrams and the fact that the larger the degree of polymerization, the higher is the crystallinity of the polymer, indicate that the polymers are substantially linear and are arranged in a regular manner.

The degree of polymerization (p) is scarcely affected by the kind of catalyst or by the length of the methylenic chain of the monomer (n), but it is strikingly influenced by whether n is odd or even (see Figs. 2 and 3, Tables I and II).

Experimental*

α,ω-Bis(4-acetylphenoxy)alkanes (I: R=H, n= 1, 2, 3, 4, 5, 6 and 10).—Sodium 4-acetylphenoxide prepared from 4-acetylphenol (15.8 g., 0.12 mol.) and a nearly equivalent amount of sodium ethoxide in ethanol, was dried under reduced pressure, mixed with dibromomethane (11.5 g., 0.066 mol.), a small amount of potassium iodide and dimethylformamide (27 ml.), and then heated under reflux for 3 hr. The cooled reaction mixture was poured into ice-water, and the solid which deposited was collected by filtration, washed with water and then recrystallized from ethanol to afford I, R=H, n=1, (15.2 g., 89%) in the form of colorless needles (m. p.

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* Melting points are not corrected.

104~105°C). IR: Nujol mull, 1680 (CO), 1275 (=C-O-) and 820 cm^{-1} (*p*-disubstituted benzene).

Found: C, 71.95; H, 5.64. Calcd. for $C_{17}H_{16}O_4$: C, 71.82; H, 5.67%.

A similar treatment of sodium 4-hydroxyacetophenone with α,ω-dibromoalkanes (n=2,3,4,5,6 and 10) yielded the following ketones:

I: R=H, n=2, colorless needles (14%), m. p. 165 °C.

Found: C, 72.40; H, 6.03. Calcd. for $C_{18}H_{18}O_4$: C, 72.46; H, 6.08%.

I: R=H, n=3, colorless needles (21%), m. p. 126 °C.

Found: C, 72.96; H, 6.44. Calcd. for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45%.

I: R=H, n=4, colorless leaflets (60%), m. p. 145.5 ~146.5°C.

Found: C, 73.44; H, 6.79. Calcd. for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79%.

I: R=H n=5, colorless leaflets (62%), m. p. 89~90°C.

Found: 74.06; H, 7.16. Calcd. for $C_{21}H_{24}O_4$: C, 74.09; H, 7.11%.

I: R=H, n=6, colorless leaflets (57%), m. p. 123 ~124.5°C.

Found: C, 74.21; H, 7.93. Calcd. for $C_{22}H_{26}O_4$: C, 74.55; H, 7.39%.

I: R=H, n=10, colorless leaflets (67%), m. p. 105 °C.

Found: C, 75.95; H, 8.35. Calcd. for $C_{26}H_{34}O_4$: C, 76.06; H, 8.34%.

α, ω-Bis (4-ethynylphenoxy) alkanes (II: R=H, n=1,2,3,4,5,6 and 10).—A mixture of I: R=H, n=1 (14.2 g., 0.05 mol.), phosphorus pentachloride (27 g., 0.13 mol.) and phosphorus oxychloride (20 ml.) was heated at 70°C for 2 hr. The crude chloride which remained after the removal of the solvent under reduced pressure was dissolved in dry ether (100 ml.), and the solution was added to sodium (10 g., 0.43 g. atom) amide in liquid ammonia (500 ml.). After the ammonia had been evaporated, the residue was decomposed with water and extracted with ether. The ethereal solution was washed with water, dried over magnesium sulfate, and evaporated. The crude crystals thus obtained were recrystallized from ethanol to give II, R=H, n=1, (7.4 g., 60%); m. p. 85.5~86°C. IR: Nujol mull, 3295 (-C≡CH), 2095(-C≡C-), 1220 (=C-O-) and 813, 833 cm^{-1} (*p*-disubstituted benzene).

Found: C, 82.19; H, 4.88. Calcd. for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87%.

Further purification of the compound for oxidative polymerization was carried out by means of column chromatography on alumina from carbon tetrachloride.

By the same method as that employed for II, R=H, n=1, the following diethynyl compounds were prepared:

II: R=H, n=2, colorless needles (37%), m. p. 170.5 °C.

Found: C, 82.80; H, 5.54. Calcd. for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38%.

II: R=H, n=3, colorless needles (36%), m. p. 124 ~124.5°C.

Found: C, 82.35; H, 5.83. Calcd. for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84%.

II: R=H, n=4, colorless needles (47%), m. p. 118.5 ~119°C.

Found: C, 82.26; H, 6.42. Calcd. for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25%.

II: R=H, n=5, colorless needles (70%), m. p. 97~98.5°C.

Found: C, 82.68; H, 6.59. Calcd. for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62%.

II: R=H, n=6, colorless leaflets (32%), m. p. 111~111.5°C.

Found: C, 82.18; H, 7.10. Calcd. for $C_{22}H_{22}O_2$: C, 82.98; H, 6.96%.

II: R=H, n=10, colorless leaflets (56%), m. p. 110 ~111.5°C.

Found: C, 82.34; H, 7.98. Calcd. for $C_{26}H_{30}O_2$: C, 83.38; H, 8.07%.

α, ω-Bis(4-acetyl-2-methylphenoxy)alkanes (I: R=CH_3, n=1,2,3,4,5 and 6).—In the same manner as that described in the preparation of II, R=H, n=1, 2-methyl-4-acetylphenol (30 g., 0.2 mol.) was first converted to its sodium derivative and then treated with dibromomethane (17.4 g., 0.1 mol.) and a small amount of potassium iodide in dimethylformamide (100 ml.) to afford I, R=CH_3, n=1. Recrystallization from ethanol gave colorless needles (10.3 g., 33%), m. p. 132.5~133.5°C. IR: Nujol mull, 1680 (CO), 1275 (=C-O-) and 815 cm^{-1} (1, 2, 4-trisubstituted benzene).

Found: C, 73.12; H, 6.44. Calcd. for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45%.

A similar treatment of sodium 2-methyl-4-acetylphenoxide with α,ω-dibromoalkanes yielded the following ketones:

I: R=CH_3, n=2, colorless needles (25%), m. p. 167~167.5°C.

Found: C, 73.34; H, 6.77. Calcd. for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79%.

I: R=CH_3, n=3, colorless leaflets (52%), m. p. 108.5~109.5°C.

Found: C, 73.98; H, 7.13. Calcd. for $C_{21}H_{24}O_4$: C, 74.09; H, 7.11%.

I: R=CH_3, n=4, colorless leaflets (64%), m. p. 114.5~115.5°C.

Found: C, 74.45; H, 7.34. Calcd. for $C_{22}H_{26}O_4$: C, 74.55; H, 7.39%.

I: R=CH_3, n=5, colorless leaflets (52%), m. p. 81.5~82.5°C.

Found: C, 74.98; H, 7.58. Calcd. for $C_{23}H_{28}O_4$: C, 74.97; H, 7.66%.

I: R=CH_3, n=6, colorless leaflets (76%), m. p. 87~88°C.

Found: C, 75.21; H, 7.90. Calcd. for $C_{24}H_{30}O_4$: C, 75.36; H, 7.91%.

α, ω-Bis(4-ethynl-2-methylphenoxy)alkanes (II: R=CH_3, n=1, 2, 3, 4, 5 and 6).—I, R=CH_3, n=1 (7.8 g., 0.025 mol.) was chlorinated with phosphorus pentachloride (11.5 g., 0.055 mol.) in phosphorus oxychloride (20 ml.) at 60°C for 2 hr., and the crude product was treated in the manner shown in the preparation of II, R=H, n=1, to yield II, R=CH_3, n=1, which was then recrystallized to give colorless needles (3 g., 44%), m. p. 138.5~139 °C. IR: Nujol mull, 3260 (-C≡CH), 2100 (-C≡C-), 890 (isolated H) and 815 cm^{-1} (1,2,4,-trisubstituted benzene).

Found: C, 82.63; H, 5.80. Calcd. for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84%. Further purification was carried out by column chromatography on alumina from carbon tetrachloride.

Using the method employed for I, R=CH_3, n=1, the following diethynyl compounds were prepared:

II: R=CH_3, n=2, colorless needles (20%), m. p. 166~167°C.

Found: C, 82.73; H, 6.25. Calcd. for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25%.

II: R=CH_3, n=3, colorless plates (46%), m. p. 67.5~69°C.

Found: C, 82.68; H, 6.63. Calcd. for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62%.

II: R=CH_3, n=4, colorless needles (38%), m. p. 103~104°C.

Found: C, 82.70; H, 6.97. Calcd. for $C_{22}H_{22}O_2$: C, 82.98; H, 6.96%.

II: R=CH_3, n=5, colorless needles (34%), m. p. 87~88°C.

Found: C, 82.69; H, 7.24. Calcd. for $C_{23}H_{24}O_2$: C, 83.10; H, 7.28%.

II, R=CH_3 n=6, colorless leaflets (71%), m. p. 91.5~93°C.

Found: C, 83.10; H, 7.61. Calcd. for $C_{24}H_{26}O_2$: C, 83.20; H, 7.56%.

3-Methyl-4-methoxyphenylacetylene (IV: R=CH_3).—A mixture of 3-methyl-4-methoxyacetophenone[5] (8.8 g., 0.053 mol.), chloroform (25 ml.), and phosphorus pentachloride (15.5 g., 0.074 mol.) was heated at 60°C for 2 hr. After the chloroform had been removed under reduced pressure, the crude product was suspended in dry tetrahydrofuran (100 ml.), and the suspension was stirred drop by drop to sodium (6 g., 0.265 g. atom) amide into liquid ammonia (300 ml.). The stirring was continued for a further 1.5 hr. After the ammonia had evaporated, the residue was decomposed with water and extracted with ether. The ethereal layer was washed with water and dried over sodium sulfate. The removal of the solvent afforded IV, R=CH_3 (3.5 g., 44%) as an oily material which partly solidified when kept standing at room temperature. The recrystallization of the solid from ethanol yielded the pure substance in the form of colorless plates; m. p. 75~77°C. IR: Nujol mull, 3295 (-C≡CH), 2095 (-C≡C-), 2850 (-OCH_3) and 898, 820 cm^{-1} (1, 2, 4-trisubstituted benzene).

Found: C, 82.41; H, 6.82. Calcd. for $C_{10}H_{10}O$: C, 82.16; H, 6.90%.

3, 3′-Dimethyl-4,4′-dimethoxydiphenyldiacetylene (V: R=CH_3).—A mixture of IV, R=CH_3, as the crude oil (1.8 g.), cupric acetate monohydrate (1.8 g.) and pyridine (20 ml.) was stirred at 55°C for 2 hr. The solvent was removed in vacuo and the residue was decomposed with water and extracted with ether. The ethereal layer was washed with water, dried over sodium sulfate and evaporated. On recrystallization of the residue from acetone V, R=CH_3, was obtained in a very high yield in the form of colorless needles (m. p. 163~165°C). IR: Nujol mull, 2140 (-C≡C-) and 890, 810 cm^{-1} (1, 2, 4-trisubstituted benzene). UV: $\lambda_{max}^{\text{Ethanol}}$, 262 (56700), 268 (58000), 281 (41000), 300 (37400), 319 (45000) and 342 mμ (ε, 36900).

Found: C, 82.51; H, 6.18. Calcd. for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25%.

4-Methoxyphenylacetylene (IV: R=H) and 4,4′-Dimethoxydiphenyldiacetylene (V: R=H).—4-Methoxyacetophenone[6] (3 g., 0.02 mol.) was treated with phosphorus pentachloride (5 g., 0.024 mol.) and then with sodium amide (0.086 mol.) in liquid ammonia to yield IV, R=H, as an oil which was used for the following coupling reaction without further purification, though it was still somewhat inhomogeneous. IR: liquid, 3300 (-C≡CH), 2850 (-OCH_3), 2140 (-C≡C-) and 835 cm^{-1} (*p*-disubstituted benzene). In the same manner as that employed for IV, R=CH_3, IV, R=H, was coupled giving quantitatively diacetylene V, R=H, in the form of colorless needles (m. p. 143.5°C). IR: Nujol mull, 2130 (-C≡C-) and 843, 822 cm^{-1} (*p*-disubstituted benzene). UV: $\lambda_{max}^{\text{Ethanol}}$, 267 (27700), 281 (28700), 299 (34000), 317 (44000) and 341 mμ (ε, 36700).

Found: C, 82.10; H, 5.37. Calcd. for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38%.

The General Procedure for the Oxidative Polymerization of II.—A mixture or II, pyridine and cupric acetate monohydrate or cuprous chloride was stirred under the conditions summarized in Tables I and II. The precipitate formed was collected by filtration, washed successively with dilute hydrochloric acid, water and methanol, and then dried in vacuo.

The Linear Dimer of 1, 6-Bis(4-ethynyl-3-methylphenoxy)hexane (II: R=CH_3, *n*=6).—When the oxidative coupling of II, R=CH_3, n=6, was carried out in methanol-pyridine (30:1) with cupric acetate monohydrate, a small amount of the linear dimer (III: R=CH_3, n=6, p=2) was produced. along with a large amount of an insoluble polymer, Colorless leaflets, m. p. 114~116°C. IR: Nujol mull, 3305 (-C≡CH), 2130, 2090 (-C≡C-) and 885, 815, 805 cm^{-1} (1, 2, 4-trisubstituted benzene). UV: $\lambda_{max}^{\text{Ethanol}}$, 269 (32200), 282 (34300), 298 (40400), 318 (40400) and 340 mμ (ε, 39800).

Found: C, 83.24; H, 7.29. Mol. wt., 699 (camphor). Calcd. for $C_{48}H_{50}O_4$: C, 83.44; H, 7.30%. Mol. wt., 695.

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[6] L. Gattermann, R. Ehrhardt and H. Maisch, *Ber.*, 23, 120 (1890).