investigation.

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Synthesis of a Nitro-Substituted Epoxy Resin from Distyryldinitrobenzene Derivatives

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ABSTRACT: A nitro-substituted epoxy resin, diglycidyl ether of 4,6-dinitro-1,3-bis(*p*-hydroxystyryl)benzene, has been synthesized and shown to be curable with an amine or an anhydride. The synthesis started with the condensation reaction of a dinitroxylene with a *p*-alkoxybenzaldehyde. The reaction proceeded readily on both methyl groups when the symmetrical 4,6-dinitro-*m*-xylene was used. The cleavage of the benzyl ether produced from the condensation with *p*-benzyloxybenzaldehyde was feasible, whereas the cleavage of the corresponding methyl ether was impractical. The bisphenol obtained appeared to be stable to oxidation. The products are probably of trans,trans configuration.

In our work on epoxy resins, we have taken an interest in the synthesis of a nitro-substituted epoxy resin by epoxidizing a bisphenol prepared from a distyrylbenzene derivative. An epoxy resin containing nitro group substituents could be used to formulate pyrotechnic binders. Also, some nitro epoxies are known to char heavily when burnt, and such charring propensity has been considered an important feature of an ablative material.[2,3] Reme reported in 1890 the condensation reaction of 2,4-dinitrotoluene with benzaldehyde.[4] Condensation of dinitroxylenes with substituted aldehydes may give distyrylbenzene derivatives which may be converted to the required bisphenol for epoxidation. The distyrylbenzene system has recently been a target of extensive investigation for its luminescence and laser-producing properties.[5-9] Many of these properties have been explored for use as scintillators[10,11] or patented as stabilizers for plastics.[12] With such interests, we describe in this paper our synthesis of a nitro-substituted epoxy resin and wish that this work may lead to the investigation of the optical properties of a series of distyrylbenzene compounds with various substitutents that can be derived from the nitro groups.

Experiment Section

Physical Methods. Infrared (IR) spectra were determined either in KBr pellets or on NaCl crystal plates with a Perkin-Elmer 467 grating IR spectrophotometer. Visible and ultraviolet (UV) absorption spectra were taken with a Cary 14 spectrometer. To obtain nuclear magnetic resonance spectra, either a Varian T-60 high-resolution NMR spectrometer or a JEOL FX-100 pulse FT spectrometer was used. The latter is equipped with a 5-mm variable temperature $^1H/^{13}C$ dual-frequency probe. For ^{13}C-NMR experiments, various irradiation modes were employed to obtain complete decoupling, off-resonance decoupling, and pulse-gated decoupling spectra. The number of scans varied between 2000 and 22000. The chemical shifts were measured relative to internal tetramethylsilane. Thermal analysis was conducted with a DuPont thermal analyzer 990 including both the differential scanning calorimetry (DSC) and the thermogravimetric analysis (TGA) modules. Melting point (mp) was determined by the capillary tube method and corrected. Elemental analysis was performed by the Galbraith Laboratories, Inc.

Materials. *p*-Hydroxybenzaldehyde and benzyl chloride were of ACS grade from Fisher Chemical; epichlorohydrin, ACS grade, from Pfaltz and Bauer, Inc.; *p*-anisaldehyde, practical grade, from Eastman Chemical; Nadic methyl anhydride (NMA), technical grade, from Allied Chemical; and 2,4-dinitro-*m*-xylene, practical grade, from Aldrich Chemical. 4,6-Dinitro-*m*-xylene was first prepared according to a known procedure[13,14] and later obtained from Aldrich Chemical (practical grade).

Condensation of 2,4-Dinitro-*m*-xylene with *p*-Anisaldehyde. A mixture of 1.96 g (10 mmol) of 2,4-dinitro-*m*-xylene (mp 84–5 °C, recrystallized from EtOH), 3.10 g (22.8 mmol) of *p*-anisaldehyde, and 10 drops of piperidine in a round-bottom flask was heated at 150 °C under reflux for 8 h with magnetic stirring. After the first and the 4th h of heating, the condenser was temporarily removed for a few minutes to evaporate the water produced in the condensation reaction. Ten more drops of piperidine were added each time to make up the loss in the evaporation periods. At the end of the reaction, the dark brown reaction mixture was poured into a beaker containing 100 mL of stirred ethanol. The alcoholic mixture was filtered. Concentration of the filtrate by vacuum evaporation gave a black slurry, the NMR spectrum of which indicated essentially a mixture of the unreacted starting materials. Purification of the alcohol-insoluble dark-brown solid (1.51 g) by elution chromatography with benzene over an alumina column yielded 1.29 g (41% yield) of 2,6-dinitro-5-(*p*-methoxystyryl)toluene (I), mp 154–5 °C. Recrystallization from benzene/hexane gave light orange needles: mp 155.8–166.8 °C; NMR ($CDCl_3$) δ 2.46 (s, 3, methyl), 3.85 (s, 3, methyoxy), 6.82 and 6.99 (s, 2, olefinic), 7.10–8.10 (m, 6, aromatic). Anal. Calcd for $C_{16}H_{14}N_2O_5$: C, 61.15; H, 4.49; N, 8.91. Found: C, 60.93; H, 4,53; N, 8.89.

Preparation of *p*-Benzyloxybenzaldehyde. A mixture of 244 g (2.0 mol) of *p*-hydroxybenzaldehyde, 265 g (2.1 mol) of benzyl chloride, 600 g (4.3 mol) of anhydrous potassium carbonate, and 1300 mL of anhydrous methyl ethyl ketone was heated under reflux for 10 h with mechanical stirring. The cooled reaction mixture was diluted with water and extracted with ether. The ether extracts were combined, washed with water and 10% NaOH solution, and dried over anhydrous K_2CO_3. Removal of the solvent by evaporation with a rotary evaporator under vacuum left an orange oil, which solidified rapidly. The solid was recrystallized from a minimum amount of ethanol to yield 292 g of *p*-benzyloxybenzaldehyde, mp 71–3 °C (lit.[15] mp 70 °C). An additional crop of 44 g, mp 70–4 °C, was obtained from the mother liquor (81% total yield): NMR ($CDCl_3$) δ 5.18 (s, 2, benzylic), 9.92 (s, 1, aldehydic), 7.00–7.95 (m, 9, aromatic). Anal. Calcd for $C_{14}H_{12}O_2$: C, 79.24; H, 5.66. Found: C, 78.99; H, 5.73.

Condensation of 4,6-Dinitro-*m*-xylene with *p*-Anisaldehyde and *p*-Benzyloxyaldehyde. The condensation reaction of 4,6-dinitro-*m*-xylene (mp 93–4 °C) with *p*-anisaldehyde was run in a manner similar to that described for 2,4-dinitro-*m*-xylene. At the end of the reaction, the reaction mixture was cooled and solidified. The solid was broken up and washed with 50 mL of hot ethanol. The collected reddish brown powder was recrystallized twice from glacial acetic acid to afford 5.5 g (63% yield) of the product, 4,6-dinitro-1,3-bis(*p*-methoxystyryl)benzene (II), mp 181–4 °C. Further purification of II by elution chromatography over a silica gel column afforded an orange solid: mp 186–8 °C (lit.[13] mp 179 °C).

Similarily, 4,6-dinitro-1,3-bis(*p*-benzyloxystyryl)benzene (III) was prepared by condensation of 4,6-dinitro-*m*-xylene with *p*-benzyloxyaldehyde. The crude product collected (82% yield) was a reddish brown solid, mp 131–3 °C. An analytical sample of III was obtained by chromatography over a silica gel column with benzene as eluent (orange crystal melting at 134–5 °C). Anal. Calcd for $C_{36}H_{28}N_2O_6$: C, 73.96; H, 4.83; N, 4.79. Found: C, 74.13; H, 4.62; N, 4.51.

Ether Cleavage of 4,6-Dinitro-1,3-bis(*p*-benzyloxystyryl)benzene (III). In a three-necked, round-bottomed, 300-mL flask equipped with a condensor, 4.08 g (7 mmol) of III was dissolved in 180 mL of a solvent mixture composed of toluene, chloroform, and methylene chloride in equal amounts. The solution was purged with nitrogen and cooled to and maintained at 0 °C with an ice bath. A stream of dry HBr gas was bubbled through the solution at such a rate that a slow but constant bubbling occurred at the water trap. The solution became cloudy first and then clear after 2 h and a layer of brown solid deposited on the wall of the flask. The HBr bubbling was continued for a total of 3 h. The mixture was stirred at room temperature for another 2 h.

After removing the excess HBr gas by brief evacuation, the supernatant liquid layer was decanted out and evaporated to near dryness with a rotary evaporator under vacuum. The solid residue and the solid deposited on the wall of the reaction flask were all dissolved in ethyl ether. The ether solutions were combined, washed with a 5% $NaHCO_3$ solution, and extracted with a 5% NaOH solution. The ether layer containing byproduct benzyl bromide was discarded. The dark brown aqueous extract was filtered. The filtrate was acidified with a 6 N HCl solution to yield an orange precipitate. The mixture was extracted with ether. The light brown ether extract was washed with a 5% $NaHCO_3$ solution and a saturated NaCl solution sucessively and filtered over anhydrous $MgSO_4$. Evaporating the solvent from the filtrate yielded 2.62 g (93 percent yield) of dark red glassy solid, 4,6-dinitro-1,3-bis(*p*-hydroxystyryl)benzene (IV). The NMR spectrum showed complete disappearance of the benzylic protons.

The bisphenol IV was found to be insoluble in methylene chloride or chloroform but soluble in ether, benzene, acetone, and methanol. Efforts to recrystallize it were unsuccessful from methanol, 2-propanol, methanol/water, or acetone/water. An analytical sample, mp 150–2 °C, was obtained by chromatography over a silica gel column with benzene as eluent. Anal. Calcd for $C_{22}H_{16}N_2O_6$: C, 65.35; H, 3.96; N, 6.93. Found: C, 65.54; H, 3.71; N, 6.70.

Diglycidyl Ether (V) of 4,6-Dinitro-1,3-bis(*p*-hydroxystyryl)benzene. In a 50-mL, three-necked, round-bottomed flask equipped with a magnetic stirrer, a condenser, and a dropping funnel, 1.62 g (4.0 mmol) of IV was dissolved in 13.0 mL of epichlorohydrin by heating to reflux with an oil bath. A solution of 0.33 g of NaOH in 1.5 mL of water was added in portion from the dropping funnel to the flask. In order to avoid possible excess exotherm, the oil bath was temporarily removed during each addition of the NaOH solution. The reaction mixture turned a dark color and some solid started to deposit on the wall when the NaOH was added. After refluxing for about 30 min, the reaction mixture was vacuum distilled to remove the excess epichlorohydrin and the water. The residue in the flask was extracted with methylene chloride. The extract was filtered. The filtrate was evaporated with a rotary evaporator under vacuum to remove the solvent and any residual epichlorohydrin. The red solid residue was dissolved in chloroform. The solution was washed with a 5% NaOH solution and dried over anhydrous Na_2SO_4. Removal of the solvent afforded 1.60 g (77% yield) of the product, diglycidyl ether (V) of IV. The reddish brown solid product contained no starting material IV as indicated by thin-layer chromatography but could not be recrystallized from many solvents tried. Its infrared spectrum showed the characteristic absorption of the epoxide group at 910 cm^{-1}. An analytical sample, pale orange solid, mp 120–3 °C, was prepared by chromatography over a silica gel column with benzene/hexane (1:1) as eluent. Anal. Calcd for $C_{28}H_{24}N_2O_8$: C, 65.12; H, 4.65; N, 5.43. Found: C, 65.40; H, 4.37; N, 5.19.

Curing Reactions of Diglycidyl Ether (V) of 4,6-Dinitro-1,3-bis(*p*-hydroxystyryl)benzene. The curing of 0.09 g of V with an excess of diethylenetriamine (DETA), a common amine curative for an epoxy, was examined both at room temperature and at 70 °C. They were mixed with the aid of a little chloroform added. The solution was spread on a pair of NaCl crystal plates and evacuated to remove the chloroform. The progress of this curing reaction was followed by IR spectroscopy. The intensity decrease of the characteristic epoxy peak at 910 cm^{-1} was essentially completed in about 1 h for the 70 °C curing and in 3 h for the room-temperature curing. The cured films obtained were brittle and insoluble in either chloroform or acetone.

A sample of 0.2 g of V was also cured with NMA and benzyldimethylamine (BDMA). They were mixed in a weight ratio of 100:66:1.2 and cured at 120 °C. The curing was followed in the same manner as above. The intensity decrease of the anhydride carbonyl peaks at 1850 and 1770 cm^{-1} and the intensity increase of the ester carbonyl at 1730 cm^{-1} were monitored to learn the degree of cure. For comparison, a sample of a conventional bisphenol A type epoxy (Epon 828 of the Shell Chemical Co.) also was cured the same way and at the same time. The curing reactions were essentially completed in the 1st h. Two more hours of heating at 120 °C plus 2 h at 150 °C effected only slight additional cure for both epoxies.

Attempted Separation of the Possible Stereoisomers of the Condensation Products. The crude condensation product, III, was purified by chromatography over an alumina column with methylene chloride as eluent. Compound III appeared as a bright orange band at the front whereas the impurities were left behind as a deep brown long band on the column. The bright orange crystals obtained from the front fraction melted at 133–144 °C (III-1). Analysis of III-1 failed by gas chromatography with either a OV-101 or a QF-1 column. Recrystallization from benzene/hexane of some of the column-chromatographed material gave samples which melted at 169–173 °C. All of the samples collected in the purification process showed NMR spectra identical to the spectrum of the crude product. DSC analysis (heating rate: 15 °C/min) revealed the difference of their thermograms as follows (sample, endo peaks, exo peaks): III-1, 135 and 162 °C, above 200 °C; III-2, 170 °C, above 200 °C; III-3, 137 and 170 °C, above 200 °C; III-4, 145 and 170 °C, above 200 °C. When III-4 was first heated in the DSC experiment to 182 °C and then cooled to room temperature and the heat program was repeated, the two endotherm peaks merged into one at 147 °C. The 147 °C endotherm peak remained unchanged when the cooling and heating cycle was repeated several times. The endotherm peak conversion was reproducible with many runs. However, both the unheated and the heated (converted) samples gave identical IR, UV, and NMR spectra.

Attempts were made also to analyze by gas chromatography IV, the bisphenol prepared from III. IV was first silylated with the Tri-Sil or Tri-Sil-DMF reagent (Pierce Chemical Co.) to convert the nonvolatile bisphenol IV into more volatile silylated phenol derivatives according to known procedures.[16] The derivatives were then analyzed by gas chromatography. Positive silylation appeared to have taken place, but no separation was achieved with either a OV-101 or a QF-1 column under various conditions. The OV-101 column was demonstrated to be good for the analysis of the silylated *o*- and *p*-nitrophenols under similar conditions. Some indications of sample decompositions were found at the glass-lined injection port.

Results and Discussion

Condensation of Dinitroxylenes with Aldehydes. Using piperidine or sodium ethoxide as catalyst, Reme

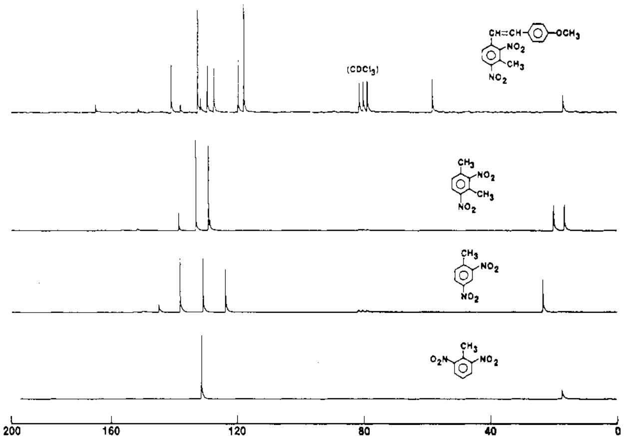


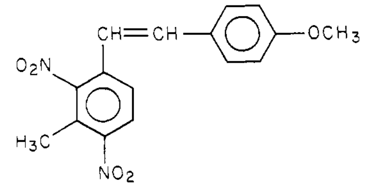
Figure 1. Proton noise decoupled ^{13}C NMR spectra (25 MHz, in ppm).

Table I
Carbon Chemical Shifts of Methyl Groups

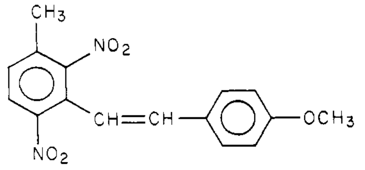
position of methyl group	chemical shift (ppm) of compd			
	I	M_1	M_2	M_3
ortho to both nitro groups	14.49	14.05		14.30
ortho and para to nitro groups		17.36	20.34	

condensed 2,4-dinitrotoluene with benzaldehyde.[4] In the presence of benzoic anhydride, Hasegawa et al. recently prepared distyrylpyrazine from dimethylpyrazine and benzaldehyde.[17] When this work was started, 2,4-dinitro-*m*-xylene was the only dinitroxylene commercially available. Efforts to condense 2,4-dinitro-*m*-xylene with *p*-hydroxybenzaldehyde and *p*-anisaldehyde either were fruitless or ended up with the formation of a monostyrylbenzene derivative (I) confirmed by elemental analysis. Catalysts tried in the experiments include piperidine, pyridine, piperidine/pyridine, benzoic anhydride, and sodium methoxide.

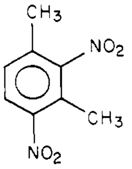
The condensation of nitroxylene with aldehyde is analogous to aldol condensation which can be catalyzed by a base. The monocondensation behavior of 2,4-dinitro-*m*-xylene appears to reflect the steric difference of its two methyl groups. In order to determine whether the structure of the monocondensation product is Ia or Ib, ^1H- and ^{13}C-NMR experiments were carried out to compare I with model compounds 2,4-dinitro-*m*-xylene (M_1), 2,4-dinitrotoluene (M_2), and 1,6-dinitrotoluene (M_3). The proton chemical shifts of the M_1's two methyl groups known in literature[18] are 2.43 ppm (singlet) for the one ortho to both nitro groups and 2.39 ppm (singlet) for the other. As close as they are, it is very difficult to identify the isomeric structures of I by simply comparing its methyl proton chemical shift (2.46 ppm) with those of M_1. However, the ^{13}C-NMR experiments revealed positive information. Figure 1 shows proton noise decoupled ^{13}C NMR spectra of I, M_1, M_2, and M_3. The methyl carbon shifts of the four compounds are recorded in Table I. Obviously, the methyl carbons ortho to both nitro groups in these compounds display more shielded chemical shifts than those ortho and para to nitro groups. The difference of the two kinds of shifts is large enough to clearly indicate that the methyl group in I is ortho to both nitro groups, and the structure of I is Ia. This structure assignment is also consistent with and hence confirmed by the coupling phenomena. Figure 2 compares the ^1H gated decoupling ^{13}C NMR spectra of I and M_1. The two quartets of M_1 are due to two methyl carbons. The methyls ortho and para to the nitro group are further coupled and hence split as shown by the neighboring ring proton. The fact that the quartet of I's methyl shows no further split confirms that the methyl is ortho to both nitro groups as in structure Ia.



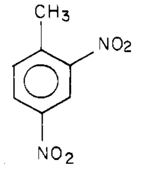
Ia



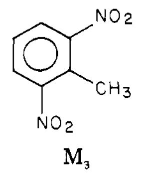
Ib



M_1



M_2



M_3

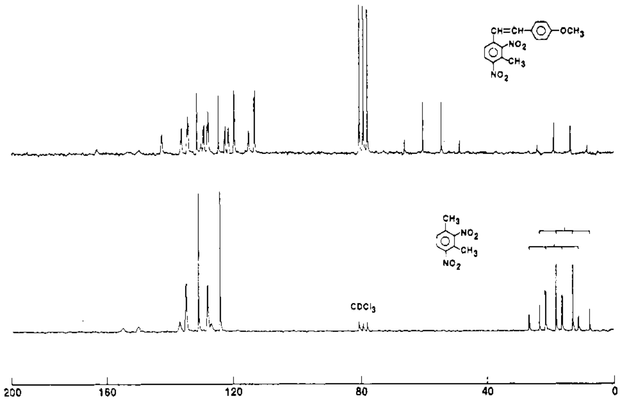


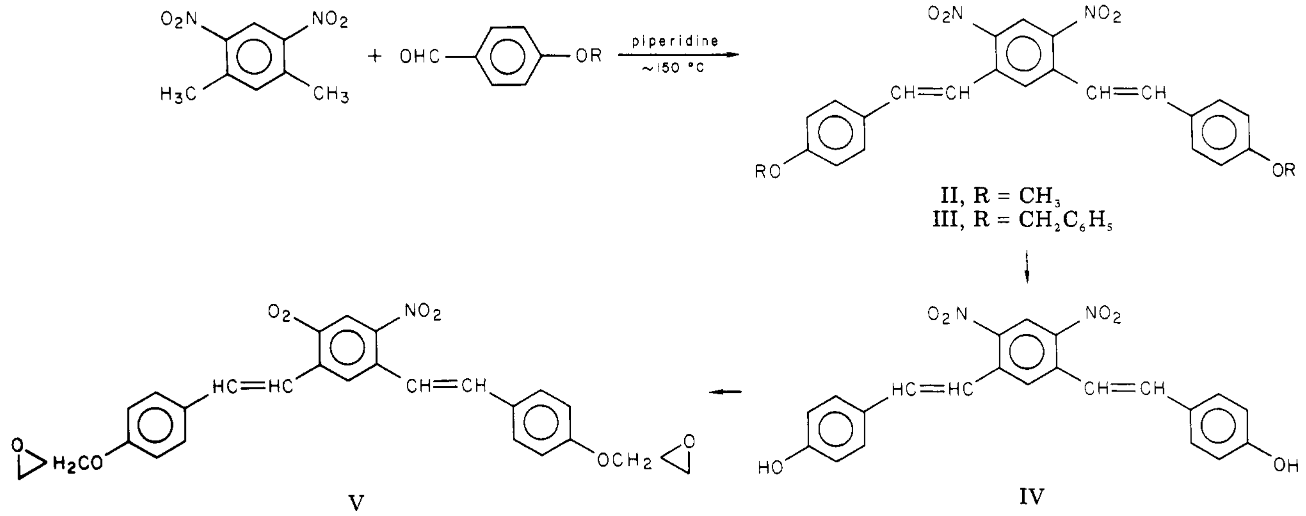
Figure 2. Proton gated decoupling ^{13}C NMR spectra (25 MHz, in ppm).

When it was realized that *p*-hydroxybenzaldehyde was not favorable due to its reaction with the catalysts, and a symmetrical dinitroxylene with less hindered methyl groups seemed to be necessary to achieve condensation at both methyl groups of the nitroxylene, 4,6-dinitro-*m*-xylene was first prepared by the nitration of *m*-xylene according to a known procedure[13,14] and later obtained from a commercial source. The symmetrical dinitroxylene was condensed at 150 °C in the presence of piperidine with *p*-anisaldehyde by the method of Ruggli et al.[13] to give II. In a similar manner, III was prepared from *p*-benzyloxybenzaldehyde with good yield. Elemental analyses and spectral data verified their structures, which will be discussed later.

The condensation reaction is the first step in the synthesis and is followed by ether cleavage and epoxidation. The complete synthetic route is described below in Scheme I.

Bisphenol by Ether Cleavage. The desired bisphenol IV was prepared by ether cleavage of the condensation products, II or III. II is a methyl ether, and cleavage of a methyl ether of a phenolic compound with an acid such as HI is known to be a common method.[19,20] However, when II was refluxed in a solution of HI/HOAc (1:1 mix),

Scheme I
Synthetic Route



only a very poor yield of IV was obtained together with some HI addition products. No cleavage reaction took place with many other reagents such as HCl, HBr, HBr/HOAc, pyridine/HCl, KOH/EtOH, $AlCl_3$, NaOEt,[21] and Grignard reagents. The difficulty encountered in the cleavage of the methyl ether led to the preparation of *p*-acetoxybenzaldehyde, *p*-acetamidobenzaldehyde, and *p*-benzyloxybenzaldehyde, but only the last aldehyde was successfully condensed with the dinitro-*m*-xylene to give a good yield of III whereas the first two aldehydes lost their protective acetyl group to the catalyst base before any condensation reaction could take place.

It was possible to cleave the benzyl ether III with HBr/HOAc, but an excellent yield was obtained by using the method of Lushchik et al.[22] The latter method involved bubbling dry HBr gas through an ice-cold solution of III in an inert solvent mixture. Attempts to apply this method to cleave the methyl ether II were not successful, however.

During the process of product isolation, some bisphenol III tended to separate from its ether solution, although in very small amounts. The separated solids could be redissolved in acetone, but some precipitate gradually appeared in the acetone solution. The IR spectra of the insolubles were, nevertheless, identical to the product remaining in solution. Some samples, in both solid state and solution, were purposely exposed to air for many days, but no change was detected spectroscopically. To further test its susceptibility to oxidation, experiments were run to oxidize III with Ag_2O in acetone,[23] $K_3Fe(CN)_6$ in dilute Na_2CO_3 solution,[24,25] and CrO_3 in acid medium (Jones reagent).[26] The first oxidizing agent is mild and was successfully used by Konig et al.[23] to effect the oxidation of 1,2-bis(*p*-hydroxyphenyl)ethene to its corresponding quinone. The second reagent is a widely used phenol oxidant through a one-electron transfer mechanism. In all cases, the starting material was recovered. The demonstrated resistance of IV to oxidation appears to reflect the stabilization effect of the nitro group substituents and also the high-energy barrier in the formation of unknown *m*-quinone structures. Apparently, the change of solubility behavior of IV is not a result of oxidation but could be caused by the intermolecular association owing to H bonding between nitro and hydroxyl groups.

Epoxidation and Curing of the Nitro-Substituted Epoxy Resin. The bisphenol IV was readily epoxidized with epichlorohydrin in the presence of sodium hydroxide. The obtained nitro-substituted epoxy resin V showed characteristic epoxide absorption at 910 cm^{-1} in its IR spectrum. The crude V, which could not be purified by recrystallization from many solvents, was separately cured with common epoxy curing agents DETA and NMA. The curing reactions were followed spectroscopically by observing the diminution of the 910-cm^{-1} absorption for the amine and the intensity decrease of the anhydride carbonyl peaks at 1850 and 1770 cm^{-1} together with the increase of the ester carbonyl at 1730 cm^{-1} for the anhydride cure. For comparison, a conventional bisphenol A-type epoxy, Epon 828, was cured at the same time with NMA. These preliminary curing experiments demonstrate positively the progress of the curing reactions, and the reactions were rapid.

DSC and TGA were run to compare the thermal behaviors of the cured V with the cured Epon 828. No distinctive rapid oxidation was shown with the nitro-substituted epoxy V. Apparently, to achieve a significant pyrotechnic property, either a curing agent containing nitro groups has to be used or the resin molecule should have more nitro group substituents. No attempt was made at this time to optimize the curing conditions or to check other cure properties.

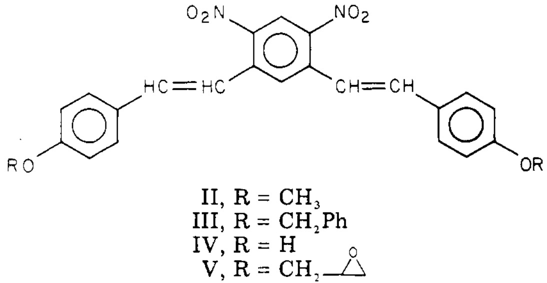
Chemical Structure. In addition to elemental analyses of the compounds synthesized, their spectroscopic data were collected to verify the structures. The NMR absorption assignments are given in Table II. The unique aromatic proton between the nitro groups can be easily identified at the low field near 8.60–8.70 ppm. The two olefinic protons are apparently not equivalent due to the presence of nitro groups on one of the two rings in proximity.[27] The two peaks assigned as olefinic protons have nearly equal intensity, each corresponding to one proton, and hence appear to represent the two protons separately. However, the possibility cannot be ruled out at this moment that they could stand for the olefinic protons of two geometric isomers since it is known that the olefinic protons of *trans*- and *cis*-stilbene appear as singlets at 7.10 and 6.55, respectively.[28]

The UV spectrum of III (sample III-4) has two maxima [$\lambda_{\max6}$ (nm), $\epsilon_{\max}$ (in CH_3CN)]: 250, 30300; 390, 31600. The absorptions fall into the pattern of the UV spectra of the *p*-distyrylbenzene derivatives known in the literature.[11,29] It is expected that the bands of III would appear at longer

Table II
Proton Chemical Shifts (60 MHz, ppm)

proton	II	III	IV	V
	compound[a]			
OR (saturated)	3.90 (s)	5.12 (s)	8.78 (s, broad)[b]	2.70–4.53 (m)
aromatic	7.28–8.08 (m)	7.27–8.05 (m)	7.36–8.40 (m)	7.28–8.00 (m)
	8.70 (s)	8.67 (s)	8.65 (s)	8.60 (s)
olefinic	6.90 (s)	6.92 (s)	6.86 (s)	6.86 (s)
	7.02 (s, broad)	7.08 (s, broad)	7.00 (s, broad)	7.00 (s, broad)

[a] Compounds II–V:



II, R = CH$_3$
III, R = CH$_2$Ph
IV, R = H
V, R = CH$_2$

Deuterated chloroform was used as solvent in the NMR experiment for all except IV for which deuterated acetone was used. [b] Identified by D$_2$O deuteration.

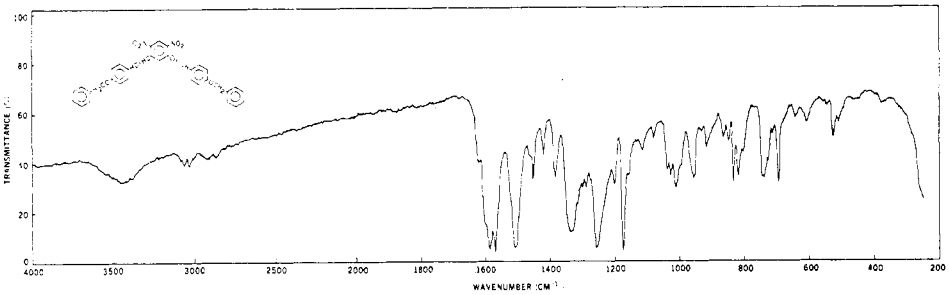
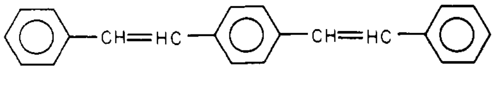


Figure 3. Infrared spectrum of 4,6-dinitro-1,3-bis(*p*-benzyloxystyryl)benzenes.

wavelengths with higher molar absorptivity than those known in the literature due to the nitro and other substituents. The absorptivity as high as shown above at both maxima certainly appears to suggest a trans,trans configuration for III.

The IR spectrum of III (sample III-4) is shown in Figure 3. The absorptions due to the aromatic skeleton vibration are complicated in the range of 1500–1600 cm^{-1} because of the presence of multiple rings and C=C bonds in conjugation. The symmetrical stretching band of the nitro group can be easily recognized at 1330–1335 cm^{-1} for all four compounds II to V. The epoxide absorption of V at 910 cm^{-1} is obvious. The out-of-plane deformation vibration of C–H is important in distinguishing the possible stereoisomers. Their absorptions, therefore, are listed in Table III, together with those of the comparable compounds known in the literature.[29] Misumi and his coworkers indicated that the 966-cm^{-1} band is typical of the trans,trans isomer, the 774-cm^{-1} band is typical of the cis,cis isomer, whereas the trans,cis isomer has both but with medium intensities. The two IR bands together with the UV spectra were used by them to study the photoisomerization of the distyrylbenzene.[30] Ito and his coworkers also employed the two deformation bands at 1015 and 740 cm^{-1} for the study of the thermal isomerizations of polyacetylene.[31] In view of all these references, it is reasonable to assume that the four compounds II to V are all trans,trans isomers. In fact, no second isomer was isolated from these compounds. In the attempted separation of the possible stereoisomers of III, samples of different melting ranges and DSC thermograms were obtained. However, they all showed identical IR, UV, and NMR spectra and, hence, appear to represent different polymorphic forms.

Table III
Out-of-Plane Deformation Vibration of Olefinic C–H

compound[a]	absorption band[b]
	
trans,trans	966 (vs)
cis,cis	966 (w), 774 (s)
trans,cis	966 (ms), 780 (m)
II	955 (m)
III	955 (m)
IV	965 (m)
V	965 (ms)

[a] The Data of the *p*-distyrylbenzene isomers are taken from "The Sadtler Standard Spectra", Sadtler Research Laboratories, Spectra No. 24046–24048. [b] Intensity notations: v = very, s = strong, w = weak, m = medium.

It is true that cis or cis,cis isomers do exist irrespective of steric hindrance in stilbene and distyrylbenzene although they are noted for being labile. However, with nitro groups so positioned as in the compounds prepared in this work, only trans,trans configuration should exist. The steric hindrance in both the cis,cis or cis,trans configurations makes them impossible to have the stable coplanar structure by resonance.

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The Organolithium Organohalide Coupling Reaction as a Synthetic Route to Poly(1,1'-ferrocenylenes)[1]

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ABSTRACT: Poly(ferrocenylenes) are synthesized by a step-growth polycoupling reaction involving 1,1'-dilithioferrocene (chelated with *N,N,N',N'*-tetramethylethylenediamine) and 1,1'-diiodoferrocene as monomers. The reactions are performed at temperatures ranging from −20 to 80 °C in ether solvents. Best results with regard to overall polycoupling efficiency (i.e., yield and molecular mass of coupling products) and product purity are obtained in a dimethoxyethane/tetrahydrofuran medium at temperatures not exceeding 25 °C. Under these conditions, the total yield of the light tan to light orange-brown, soluble poly(ferrocenylenes) amounts to more than 85%, and the number-average molecular mass of the highest molecular fraction constituting some 16% of total product approaches 4000. The addition, at early stages, of catalytic amounts of Cu(II) or Pd(II) salts to the reaction mixture with a view toward utilizing the intermediacy of reactive organocopper or organopalladium species does not lead to further substantial increases in the overall degree of polymerization. Subfractionation from benzene solution under anaerobic conditions gives subfractions with $\bar{M}_n$ in the 1000–10000 range. Preliminary magnetic susceptibility measurements indicate the polymers to be less contaminated by paramagnetic impurities than the poly(ferrocenylenes) synthesized in previous investigations, an observation of critical importance for future electrophysical studies. Spectroscopic data, supported by the results of nonpolymeric model reactions providing evidence for the absence of a ferrocyne mechanism indicate that propagation proceeds without loss of the heteroannular substituent disposition on the reactants and so are in agreement with a structural representation (**3**) implying a 1,1' type of unit interconnection along the polymer chain.

The problem of biaryl formation through coupling of aryllithium with haloarenes has been a topic of continued research interest ever since Gilman's and Wittig's pioneering work[3] on arene metalation and the no less significant contributions, mostly by Wittig, Roberts, and Huisgens, in the chemistry of dehydrobenzene (aryne).[4] With the proper choice of solvent and halogen substituent, biaryl formation may proceed to yields of 70% and higher, rendering this type of coupling reaction under favorable conditions a useful synthetic tool in the preparation of simple and mixed biaryls.

In the course of our continuing program aimed at the synthesis of compositionally pure poly(metallocenylenes)[2,5] for electrophysical and intervalence transfer studies, we investigated, as a logical outgrowth of aryl coupling chemistry, the interaction of lithio- and haloferrocenes.

Although ferrocenyl halides must be rated as poor substrates in nucleophilic substitution reactions by addition–elimination because of the appreciable basicity of the metallocene nucleus, the lithioferrocenes, especially when chelated for enhanced nucleophilicity with TMEDA (tetramethylethylenediamine),[6] should function as excellent nucleophiles in metallocenyllithium/halometallocene reactions. In one of the more recent studies of aryl–aryl coupling involving the reaction of phenyllithium with the four *p*-halotoluenes in the presence or absence of amine catalysts and TMEDA chelating agents, the fluoro-, chloro-, and bromotoluenes were found to couple through an elimination–addition sequence (benzyne mechanism), and only the iodo compound underwent direct displacement concurrently with the elimination–addition process.[7] Although no systematic studies of the coupling behavior of the haloferrocenes under similar conditions have been reported, limited information is available on the metalation chemistry of chloroferrocene. Thus, treatment of chloroferrocenes with alkyllithium

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