chemical shift, −257, in isomer IIa. As the temperature increases, the chemical shifts of the hydroxyl hydrogens move to higher field values as expected for hydrogen-bonded systems. It was also observed that J_{XY} and δ_{XY} were somewhat temperature dependent for isomer IIb, whereas for isomer IIa both J_{XY} and δ_{XY} were nearly constant over the temperature interval investigated. The observed chemical shift effects are consistent with intramolecular hydrogen bonding, and the effect of temperature on ν_{OH} seems to indicate a greater degree of hydrogen bonding in IIb, probably intramolecular, than in IIa.

The data presented for the amine-alcohols are consistent with the specific assignments of the *threo* and *erythro* structures of the individual alcohols, but the basis for the assignments is strengthened by the fact that the alcohol data lend support to the much stronger case of assignments made for the individual isochromans; thus the latter mutually support the amine–alcohol structure assignments.

Experimental[13]

Synthesis of *erythro* and *threo* Isomers IIa and b.—To 15.8 g. (0.07 mole) of 2-benzylbenzyldimethylamine (I) was added 55 ml. (0.08 mole) of approximately 1.5 *M* *n*-butyllithium in hexane, followed by ether; the metalation mixture was allowed to stand at room temperature for 6 hr. as described recently.[2] The resulting dark red solution of lithioamine I′ was poured into a boiling ether solution of 9.55 g. (0.09 mole) of benzaldehyde. After standing at room temperature for 6 hr., the reaction mixture was decomposed with 150 ml. of water, and the layers were separated. The ether layer was dried over anhydrous magnesium sulfate, and the solvent was removed. The resulting yellow oil was stirred with pentane to precipitate white crystals, which were collected on a funnel and washed free of the oil with pentane. After drying, 6.4 g. (28%) of *threo*-2-(*o*-dimethylaminomethylphenyl)-1,2-diphenylethanol (IIb), m.p. 131–137°, was obtained. Recrystallization of the product from pentane–absolute ethanol raised the melting point to 139–140°, which was not changed on further recrystallization.

Anal. Calcd. for $C_{23}H_{25}NO$: C, 83.34; H, 7.60; N, 4.23. Found: C, 83.43; H, 7.78; N, 4.23.

The combined pentane filtrate and washings was cooled to precipitate a sticky oil, which failed to crystallize. The mixture was dissolved in 250 ml. of ether and extracted three times with 2 *M* hydrochloric acid. The combined acid extracts were cooled and made basic with 6 *M* sodium hydroxide. The basic mixture was extracted with ether and the combined extracts were dried over anhydrous magnesium sulfate. Removal of the solvent afforded an oil which was crystallized from pentane. The crystals were collected and dried to give 7.0 g. (30%) of *erythro*-2-(*o*-dimethylaminomethylphenyl)-1,2-diphenylethanol (IIa), m.p. 71–78 and 77–79° after recrystallization from pentane containing a few drops of absolute ethanol.

Anal. Calcd. for $C_{23}H_{25}NO$: C, 83.34; H, 7.60; N, 4.23. Found: C, 83.59; H, 7.74; N, 4.41.

Conversion of IIa and b to Isochromans IIIa and b through the Methiodides.—These reactions were effected by adaptations of earlier procedures for related reactions.[2]

erythro isomer IIa (3.3 g., 0.01 mole) was refluxed with excess methyl iodide in 100 ml. of acetonitrile for 1 hr. After cooling, the solution was added dropwise to 500 ml. of ice-cold anhydrous ether to precipitate 4.2 g. (89%) of the corresponding methiodide (slightly hygroscopic). This methiodide (3.95 g., 0.084 mole) was cyclized at 200–210° under nitrogen[2] (30 min.). After cooling, the reaction mixture was boiled with several portions of anhydrous ether to remove the soluble isochroman from the insoluble trimethylammonium iodide. The combined ether extract was dried over anhydrous magnesium sulfate, and the solvent was removed. The residue was recrystallized from absolute ethanol to give 2.4 g. (75%) of *erythro*-3,4-diphenylisochroman (IIIa), m.p. 113–115°.

Anal. Calcd. for $C_{21}H_{18}O$: C, 88.08; H, 6.34. Found: C, 88.30; H, 6.13.

threo isomer IIb (4.4 g., 0.013 mole) was refluxed with excess methyl iodide in 150 ml. of acetonitrile for 1.5 hr. The solution was cooled, and 6.05 g. (99%) of the methiodide was precipitated by dropwise addition of 750 ml. of anhydrous ether. This methiodide (6.00 g., 0.012 mole) was cyclized as described above for the *erythro* isomer to give, after recrystallization from ethanol, 3.0 g. (81%) of *threo*-3,4-diphenylisochroman (IIb), m.p. 118–120°.

Anal. Calcd. for $C_{21}H_{18}O$: C, 88.08; H, 6.34. Found: C, 88.11; H, 6.31.

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[13] Melting points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were recorded using a Perkin-Elmer Infracord 137. Nuclear magnetic resonance spectra were obtained on a Varian A-60 n.m.r. spectrometer equipped with a variable-temperature probe. The concentrations of the samples used for n.m.r. studies were 0.4–0.5 *M* in carbon tetrachloride.

Equilibration of *para*-Substituted Styrenes to Produce *p*-Xylylenes

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P.m.r. and infrared data are presented for the formation of α-cyano-α-phenyl-α′-methyl-*p*-xylylene and its subsequent trapping through polymerization upon basic equilibration of *p*-(vinylphenyl)phenylacetonitrile. This reactive intermediate was also produced and isolated as its polymer in the basic 1,6-elimination of hydrogen chloride from α-cyano-α-phenyl-α′-methyl-α′-chloroxylene.

para-Substituted styrenes such as I and corresponding substituted *p*-xylylenes II[1b] are isomeric and in theory can be interconverted by a simple proton shift. Although analogous systems are known in which at equilibrium the quinoid form can be detected,[2] no evidence for conversion of a *para*-substituted styrene to the corresponding xylylene has been reported. A reason for this can be obtained by making a crude estimate of the equilibrium constant in the simplest styrene–xylylene system. Based on the calculated resonance energy differences of styrene (2.43β)[3] and *p*-xylylene (1.93β),[4] an equilibrium constant of 10^6 is obtained. This large equilibrium constant helps to account for the absence of evidence for the formation of α-methyl-*p*-xylylene in studies on the *p*-vinylbenzyl anion, al-

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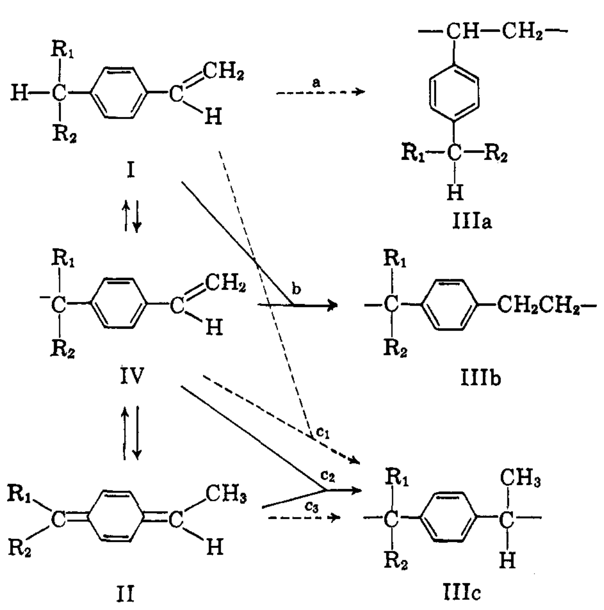
[1] (a) Correspondence regarding this paper should be sent to the Library, Union Carbide Corp., Plastics Division, Bound Brook, N. J. 08805. (b) Indexed as *p*-quinomethans or substituted 1,4-cyclohexadienes.

[2] J. A. Berson and M. Pomerantz, *J. Am. Chem. Soc.*, **86**, 3896 (1964); W. R. Roth, *Tetrahedron Letters*, **No. 17** 1009 (1964); D. F. Vaber and W. Lwowski, *J. Am. Chem. Soc.*, **85**, 646 (1963); R. B. Davis, L. C. Pizzini, and J. D. Benigni, *ibid.*, **82**, 2913 (1960).

[3] G. Berthier and B. Pullman, *Bull. soc. chim. France*, 554 (1948).

[4] C. A. Coulson, D. P. Craig, A. Maccoll, and A. Pullman, *Discussions Faraday Soc.*, **2**, 35 (1947).



though the presented data support a contribution of the *p*-quinoid resonance form to the structure of the anion.[5] An equilibrium more favorable to the xylylene can presumably be obtained by stabilizing the *p*-xylylene structure II relative to the styrene with aryl substituents (R_1 and R_2). In this light it is interesting to note that a compound presumed to be II (R_1, R_2 = $-C_6H_4C_2H_5$) apparently does not spontaneously rearrange to the corresponding styrene.[6]

In the present work the styrene I (R_1 = CN and R_2 = C_6H_5) was equilibrated under basic conditions and evidence for the formation of the xylylene II (R_1 = CN and R_2 = C_6H_5) was found. This intermediate was also isolated as its polymer in the basic 1,6-elimination of hydrogen chloride from the corresponding chloroxylene.

Experimental[7]

Acetylation of Diphenylacetonitrile.—To a stirred solution of 55 g. (0.28 mole) of diphenylacetonitrile, 18 ml. (0.26 mole) of acetyl chloride, and 100 ml. of carbon disulfide was added at 0–5° 120 g. (0.90 mole) of aluminum chloride. The mixture was stirred and refluxed for 3 days, poured into ice and hydrochloric acid, extracted with ether, washed, dried, and distilled. The crude ketone, b.p. 130–170° (0.5 mm.), 29 g., was fractionally crystallized from methanol to give 9 g. of (*p*-acetylphenyl)phenylacetonitrile, m.p. 94–95°, having characteristic vibrations at 12.01, 13.34, and 14.21 (*para*-substituted benzene and phenyl) and 4.45 μ (C≡N stretching).

Anal. Calcd. for $C_{16}H_{13}NO$: C, 81.67; H, 5.57; N, 5.95. Found: C, 81.39; H, 5.69; N, 6.09.

The *meta* isomer isolated from the mother liquors, m.p. 75–77°, absorbed at 12.69, 13.15, 13.90, and 14.40 μ (*meta*-substituted benzene and phenyl).

Anal. Found: C, 81.68; H, 5.47; N, 5.62.

(*p*-Vinylphenyl)phenylacetonitrile.—Twenty grams of (*p*-acetylphenyl)phenylacetonitrile was reduced to the alcohol with 4 g. of sodium borohydride in methanol. After extraction and washing, distillation yielded 15 g. of a viscous oil, b.p. 165–175° (0.3 mm.), $n^{25}\text{D}$ 1.5788, which could not be crystallized. Characteristic infrared absorptions were found at 2.93 (OH stretching), 4.46 (–C≡N stretching), 11.95 (*para*-substituted benzene), and 13.5 and 14.38 μ (phenyl group).

Anal. Calcd. for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90. Found: C, 80.93; H, 6.46; N, 6.07.

This alcohol, 8.0 g., was dehydrated at 230° (1 mm.) with 0.2 g. of potassium acid sulfate in the presence of a few crystals of hydroquinone. The crude distillate, 4.0 g., was recrystallized from methanol to give pure (*p*-vinylphenyl)phenylacetonitrile, m.p. 82.5–84°. The infrared spectrum showed characteristic absorptions at 4.47 (–C≡N), 6.13 (–C=C–), 10.14 and 10.96 ($-C=CH_2$), 11.95 (*para*-substituted benzene), and 13.87 and 14.39 μ (phenyl). The n.m.r. spectrum[8] showed absorptions at 304 [ArC(CN)*H*], 308, 319, 332, 349, 386, 397, 403, 414 (ArC*H*=C*H*$_2$), and 437 c.p.s. (aromatic) in the correct ratio. Oxidation with acidic dichromate gave *p*-benzoylbenzoic acid identified by mixture melting point and infrared spectrum.

Anal. Calcd. for $C_{16}H_{13}N$: C, 87.64; H, 5.97; N, 6.38. Found: C, 87.52; H, 5.98; N, 6.56.

Radical polymerization of this styrene at 150° with 1% cumene hydroperoxide catalyst gave a polystyrene-type polymer having no methyl absorptions in the infrared region (7.25 μ). After reprecipitation from acetone with methanol the polymer softened, 110–120°. The n.m.r. spectrum[8] of the polymer in deuterated chloroform had an absorption at 302 c.p.s. [ArC(CN)*H*], a broad asymmetrical peak extending from 50 to 170 with a maximum around 85 (–C*H*ArC*H*$_2$), and a broad aromatic proton absorption with a sharp peak at 435 c.p.s. The ratio of acetonitrile, backbone, and aromatic protons was found to be 1:2.9:9.4 (theoretical 1:3:9).

Anal. Calcd. for $(C_{16}H_{13}N)_n$: N, 6.38. Found: N, 6.39.

The broad asymmetric absorption at 50–170 c.p.s. is typical of low molecular weight polystyrene.[9] Its shape could be duplicated by two symmetrical peaks with maxima at 120 and 85 c.p.s. having an area ratio of 1:2 corresponding to the backbone CH and CH_2 groups.

Isomerization of *p*-Styrenes to *p*-Xylylenes.—(*p*-Vinylphenyl)phenylacetonitrile, 2.0 g. (0.0096 mole), was refluxed overnight under argon in 10 ml. of anhydrous *t*-butyl alcohol containing 0.0044 mole of potassium *t*-butoxide. The polymeric product, 1.5 g., was recovered by pouring the red reaction mixture into water and washing the resultant precipitate with water and methanol. The crude product was purified by reprecipitation from acetone into cyclohexane and from methylene chloride into petroleum ether (b.p. 40–60°) to yield 0.8 g. of polymer softening at about 190°.

Anal. Calcd. for $(C_{16}H_{13}N)_n$: C, 87.64; H, 5.97; N, 6.38. Found: C, 87.23; H, 5.85; N, 5.94.

This polymer had a reduced viscosity in benzene (0.2 g./100 ml.) of 0.05 (25°). The infrared spectrum, in addition to characteristic absorptions at 4.45 (C≡N), 12.03 (*para*-substituted benzene), and 13.5 and 14.4 (phenyl), showed an absorption at 7.26 μ (CH symmetrical deformation characteristic of $C-CH_3$). The p.m.r. spectrum[8] in deuteriochloroform showed no fine structure (even at 100° in chlorobenzene) but had broadened aliphatic peaks with maxima at 94, 160, 230, and 304 c.p.s. in the relative approximate ratios of 2.9:1.4:1.0:0.03 and in the aromatic region at 421 and 437 c.p.s. The ratio of aromatic to aliphatic hydrogens in various samples was found to be between 8:4 and 10:4 (theoretical 9:4).

A similar isomerization carried out at room temperature resulted principally in recovery of starting styrene after 2 days. After 30 days a polymer was obtained similar to that described above (including a $C-CH_3$ absorption at 7.25 μ in the infrared region) having a reduced viscosity of 0.06 and a number average molecular weight (ebullioscopic in xylene) of 3000, indicating a degree of polymerization of about 14.

The isomerization was also carried out using 0.44 g. of styrene and 2 ml. of a methanol solution containing 0.6 g. of sodium per 50 ml. After refluxing for 1 week under argon the insoluble polymer was recovered. This material had an absorption at 7.25 ($C-CH_3$) but also a second nitrile band at 4.61 μ indicating conjugation of the nitrile.

Refluxing 1 g. of the styrene with 4 ml. of a cyclohexanol solution containing 0.5 g. of sodium per 75 ml. for 16 hr. also gave a polymer which upon neutralization with hydrochloric acid and precipitation with petroleum ether gave material absorbing at 5.95 (C=O) and 7.25 μ ($C-CH_3$) in addition to the characteris-

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(5) H. Pines and J. Shabtai, *J. Org. Chem.*, **26**, 4220 (1961).

(6) C. S. Marvel, M. B. Mueller, C. M. Himel, and J. F. Kaplan, *J. Am. Chem. Soc.*, **61**, 2772 (1939).

(7) Melting points and boiling points are uncorrected.

(8) P.m.r. spectra were supplied by Dr. W. F. Beach and Miss J. C. Engeman using a Varian A-60 60-Mc. spectrometer at ambient temperature. Zero field was set at the absorption peak for tetramethylsilane and the reported shifts are downfield.

(9) F. A. Bovey, G. V. Tiers, and G. Filipovich, *J. Polymer Sci.*, **38**, 73 (1959).

tic nitrile and aromatic bands. Attempts to purify this product by reprecipitation resulted in the formation of a finely dispersed oil, indicating the material to be of very low molecular weight.

Deuterium Exchange.—(*p*-Vinylphenyl)phenylacetonitrile, 0.5 g., was dissolved in 5 ml. of deuterated methanol (OD) containing 0.4 g. of potassium hydroxide, and the solution was allowed to stand for 15 min. under argon. The product, recovered by addition of deuterium oxide and filtration of the precipitate, was similar to starting styrene. The p.m.r. spectrum[8] indicated the absence of only the proton adjacent to the nitrile group (304 c.p.s.). The infrared spectrum was similar to that of the starting styrene except for the absence of the weak peaks at 3.40 (C–H stretching) and 7.48 μ (C–H deformation).

In addition several of the weaker peaks as well as the strong phenyl absorption at 13.87 μ were shifted significantly (*i.e.*, 13.87 → 14.05, 12.90 → 13.40, 12.10 → 12.40, 9.23 → 9.45 μ).

A second equilibration carried out over a period of 16 hr. again indicated no exchange of deuterium in the vinyl protons of the recovered styrene (the experimentally detectable limit was 10% exchange of any proton), although after this period of time the recovered styrene was contaminated with some polymer.

(*m*-Vinylphenyl)phenylacetonitrile.—(*m*-Acetylphenyl)phenylacetonitrile was reduced with sodium borohydride as previously described for the *para* isomer. The crude alcohol, a viscous oil, was similarly dehydrated with potassium acid sulfate to produce an uncrystallizable oil, $n^{25}\text{D}$ 1.5948, which absorbed characteristically or strongly in the infrared region at 4.47 ($C{\equiv}N$), 6.14 ($C{=}C$), 10.15 and 10.95 ($—CH{=}CH_2$), and 12.57, 12.98, 13.20, and 14.38 μ (*meta*-substituted benzene and phenyl).

Anal. Calcd. for $C_{16}H_{13}N$: C, 87.64; H, 5.97; N, 6.38. Found: C, 87.18; H, 6.19; N, 6.49.

Attempted Isomerization of (*m*-Vinylphenyl)phenylacetonitrile.—(*m*-Vinylphenyl)phenylacetonitrile, 2.0 g. (0.009 mole) was dissolved in 10 ml. of 0.38 *M* potassium *t*-butoxide in *t*-butyl alcohol and the red-orange solution was refluxed under argon for 20 hr. The reaction mixture was poured into methanol, neutralized with acetic acid, filtered, and washed successively with methanol, water, and methanol. The yield of low polymer softening at about 80° was 0.4 g. The infrared spectrum showed characteristic absorptions at 4.50 ($C{\equiv}N$), 12.60 (*meta*-substituted benzene), and 13.30 and 14.40 μ (phenyl). Weak, somewhat broadened absorptions were found at 10.0 and 11.0 μ ($—CH{=}CH_2$), but no absorptions were observed at 7.25 μ ($C—CH_3$). The proton magnetic resonance spectrum[8] showed principal absorptions at 162, 435, and 444 c.p.s. and very weak absorptions at about 306, 312, 336, 352, 390, and 400 c.p.s., characteristic of the vinyl and acetonitrile protons. The experimental ratio of aliphatic to aromatic protons was approximately 4:9.7. Because of the broadness of the peaks and the low signal to noise ratio this ratio is within experimental error of the theoretical (4:9).

Ultraviolet Spectra.—The ultraviolet spectra of (*m*- and *p*-vinylphenyl)phenylacetonitrile were observed in methanol solution using a Cary Model 14 recording spectrophotometer. The *para* isomer absorbed strongly at 253 mμ (log ϵ 4.34), whereas the *meta* isomer absorbed maximally at 250 mμ (log ϵ 4.17). In addition the *para* isomer showed weak maxima shoulders, or inflections, at 294, 284, 275, and 262 and the *meta* isomer at 294.5, 284.5, and 275 mμ. Diphenylacetonitrile absorbs at (log ϵ in parentheses) 267 (2.28), 264 (2.51), 258 (2.61), 252 (2.54), 247.5 (2.40), and 242 (2.25). In 1 *N* methanolic potassium hydroxide the *p*-styrene turns pink due to an absorption at 485 mμ, the *meta* isomer remains colorless, and diphenylacetonitrile turns pink due to an absorption at 484.5 mμ.

Model Compounds.—2,2,4-Triphenylbutyronitrile was prepared as follows. To a solution of potassium *t*-butoxide in *t*-butyl alcohol [4.0 g. (0.102 g.-atom) of potassium in 150 ml. of dry *t*-butyl alcohol] was added consecutively with stirring 19 g. (0.098 mole) of diphenylacetonitrile and 19 g. (0.102 mole) of 2-phenylbromoethane. The reaction mixture was stirred for 24 hr., neutralized with dilute sulfuric acid, and diluted with water. The resulting organic material was triturated with methanol and the precipitated product was recrystallized from methanol, m.p. 104–106°, 15 g.

Anal. Calcd. for $C_{22}H_{19}N$: C, 88.85; H, 6.44. Found: C, 88.79; H, 6.35.

The infrared spectrum had characteristic bands at 4.53 ($C{\equiv}N$) and very strong bands at 13.32, 14.32, and 14.50 μ (phenyl groups). The p.m.r. spectrum[8] had absorptions at 428, 431, and 434 in the aromatic region and at 158 c.p.s. (single peak) in the aliphatic region. The ratio of aromatic to aliphatic protons was 15.0:4.02 (theoretical 15:4).

2,2,3-Triphenylbutyronitrile was prepared by the method of Hauser and Brasen[10] and had proton absorptions[8] at 427 and 424 (phenyl group), 232 (quartet), and 93 c.p.s. (doublet).

2,3-Diphenylbutane was prepared by the method of von Braun, Grabowski, and Kirschbaum,[11] and had proton absorptions[8] at 434 (phenyl), 167 (quartet), and 60 c.p.s. (doublet).

Poly-α-cyano-α-phenyl-α'-methylxylylene.—α-Cyano-α-phenyl-α'-methyl-α'-hydroxyxylene (3 g.) was converted to the chloride by stirring in 10 ml. of anhydrous ether with 2 ml. of thionyl chloride and evaporating the volatiles at 30° *in vacuo*. The crude concentrate was poured into a stirred solution of 5 g. of potassium hydroxide (85+%) in 40 ml. of methanol at room temperature. The precipitate which formed immediately was washed with methanol, water, and methanol, and dried. The amorphous polymer, reduced viscosity (0.2 g./100 ml., chloroform, 25°) 0.11, was swollen but in part insoluble in acetone and softened at about 200°. The acetone-insoluble portion had a reduced viscosity of 0.60 (benzene, 25°) and softened above 250°. The infrared spectrum confirmed the xylylene structure by indicating the presence of methyl groups at 7.25 μ.

Anal. Calcd. for $(C_{16}H_{13}N)_n$: C, 87.64; H, 5.97; N, 6.38. Found: C, 86.67; H, 6.16; N, 6.40.

The n.m.r. spectrum in deuteriochloroform showed three broad areas of absorption at 87, 222, and 442 and 420 c.p.s. in the relative ratio of 3.1:1.2:9.0.

9-Cyanomethylanthracene.—To a solution of 28 g. of sodium cyanide in 500 ml. of dimethylformamide (containing about 1% water) at 120–140° was added 80 g. of 9-chloromethylanthracene in 500 ml. of dimethylformamide. Heating was continued for 1 additional hr. and the mixture was poured into ice and water. The crude nitrile was removed by sublimation and crystallized from a toluene–heptane mixture to yield 50 g. of 9-cyanomethylanthracene as pale yellow crystals, m.p. 163–165°, which fluoresced yellow-green.

Anal. Calcd. for $C_{16}H_{11}N$: C, 88.45; H, 5.10; N, 6.45. Found: C, 88.71; H, 5.16; N, 6.40.

The ultraviolet spectrum had maxima at 391 mμ (log ϵ 3.93), 371 (3.97), 352 (3.79), 335 (3.49), 320 (3.11), and 257 (5.22).

Attempted Preparation of 9-Cyanomethyl-10-vinylanthracene.—To a solution of 50 g. of 9-cyanomethylanthracene and 120 ml. of acetyl chloride in 350 ml. of carbon disulfide at 0° was added with stirring 130 g. of anhydrous aluminum chloride. The reaction was allowed to warm to room temperature and stirred an additional 4 hr. The mixture was poured onto a mixture of hydrochloric acid and ice, the solvent was allowed to vaporize, and the solid product was collected by filtration. The crude product was purified by solution in acetone and reprecipitation with water, followed by sublimation and recrystallization (with charcoal) of the sublimate from xylene–heptane, xylene, and finally methyl ethyl ketone. The yield of fluffy yellow needles which fluoresced yellow, m.p. 220–222°, was 19 g. The ultraviolet spectrum had maxima at 405 mμ (log ϵ 3.58), 385 (3.54), 364 (3.67), 345 (3.60), 328 (3.36), 274 (4.40), and 253.

Anal. Calcd. for $C_{18}H_{13}ON$: C, 83.37; H, 5.05; N, 5.40. Found: C, 83.77; H, 5.03; N, 5.36.

To 200 ml. of methanol at 20° was added 19 g. of 9-cyanomethylacetylanthracene. Reduction with 5 g. of sodium tetrahydridoborate proceeded exothermically, the temperature being allowed to rise to 40°. The reaction could be followed by the disappearance of the yellow color. The crude alcohol was isolated by diluting the reaction mixture with water and filtering. Yield of the light tan alcohol which fluoresced blue after recrystallization from toluene was 18 g., m.p. 148–150°. The ultraviolet spectrum had maxima at 387 mμ (log ϵ 3.74), 3.66 (3.79), 349 (3.63), 333 (3.38), 317 (3.00), and 2.60 (5.25).

Anal. Calcd. for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N, 5.36. Found: C, 83.51; H, 6.22; N, 4.84.

This alcohol, 0.5 g., was oxidized with 6 g. of sodium dichromate in 35 ml. of glacial acetic acid by refluxing for 6 hr. The material isolated upon dilution with water melted (290°) and was shown by mixture melting point and infrared spectrum to be anthraquinone-2-carboxylic acid.

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[10] C. R. Hauser and W. R. Brasen, *J. Am. Chem. Soc.*, **78**, 82 (1956).

[11] J. v. Braun, A. Grabowski, and G. Kirschbaum, *Ber.*, **46**, 1266 (1913).

Discussion and Results

The styrene I (R_1 = CN, R_2 = C_6H_5) was prepared by acetylation of diphenylacetonitrile, reduction of the isolated *p*-ketone, and 1,2-dehydration of the resultant alcohol. This styrene appeared particularly suited for equilibration as its substituents (CN and C_6H_5) stabilize the xylylene while not contributing materially to the stability of the styrene system. In addition, the cyano group significantly increases the acidity of the adjacent protons (pK_a of phenylacetonitrile is reported to be 15.7[12]) thus facilitating the basic equilibration. Potassium *t*-butoxide, a base sufficiently strong to allow essentially complete ionization of the acetonitrile proton, was used as the catalyst and *t*-butyl alcohol was the solvent. In addition to providing a homogeneous medium, this solvent provided a high concentration of labile protons combined with a low reactivity toward nitrile groups.

Equilibration of the styrene I (R_1 = CN, R_2 = C_6H_5) in refluxing *t*-butyl alcohol for 16 hr. resulted in the formation of soluble polymer having the correct elemental composition for an addition polymer of structure IIIa, b, or c. Production of a xylylene II would be expected to result in a polymeric product as all but some tetrasubstituted *p*-xylylenes readily polymerize at room temperature. However, in addition to homopolymerization of xylylene to give IIIc (route c_3), polymer can be formed by several other processes. Anionic-initiated vinyl polymerization of the styrene (route a) can give rise to the structure IIIa. In the presence of a large amount of proton donor such as *t*-butyl alcohol a more logical polymer structure is that of IIIb. This arises through the addition of the anion IV to the styrene I with subsequent proton abstraction from solvent (route b) rather than chain propagation by the resultant anion (route a). The structure IIIc can also arise by the Michael addition of the anion IV to the xylylene II (route c_2) or by the addition of the anion IV to the α-position of the styrene I followed by proton abstraction by the resultant carbanion (route c_1).

The various polymer structures IIIa, b, and c can be distinguished in soluble polymers by means of their p.m.r. spectra. Although the polymer peaks are broadened and fine structure lost, presumably due to restricted rotation, their position can be determined reasonably accurately. A list of reference frequencies obtained from model systems is given in Table I. Based on these values, the polymer formed upon equilibration of the *p*-styrene I (R_1 = CN and R_2 = C_6H_5) was found to consist of repeating units having 25% of IIIb and 75% of IIIc, joined in a head-to-tail structure. In addition to these principal peaks in the polymer n.m.r. spectrum a low-intensity broad absorption was observed in the 300–350-c.p.s. region[8] which accounted for approximately 5% of the aliphatic protons. Assuming this included the two terminal vinyl protons and the acetonitrile proton and that the polymer is terminated by a vinyl group at one end and an acetonitrile group at the other, the molecular weight of the polymer can be estimated as approximately 3000. This is in agreement with an ebullioscopically determined molecular weight and supports a linear polymer structure. The presence of structure IIIc in the polymer is confirmed by the infrared spectrum which contains an absorption at 7.26 μ characteristic of the CCH_3 group (CH symmetrical deformation). This absorption was also found in polymers produced in systems based on methanol and on cyclohexanol, demonstrating that this absorption is not due to incorporation of solvent or catalyst in the polymer. The high softening temperature (190°) of the polymer also supports the presence of large amounts of the rigid structure IIIc and eliminates the possibility of a large fraction of IIIa which softens at 110–120°.

TABLE I

N.M.R. ABSORPTIONS FOR KNOWN SYSTEMS[a]

Structure	Proton	Positon of peak, c.p.s.	Peak multiplicity
IIIc[b]	$-\mathrm{C}H_3$	60	2
IIIa	$-\mathrm{CHC}H_2-$	85[c]	. . .
IIIc[d]	$-\mathrm{C}H_3$	93	2
IIIa	$-\mathrm{C}H\mathrm{CH}_2-$	120[c]	. . .
IIIb	$-\mathrm{C}H_2\mathrm{C}H_2-$	162	1
IIIc[b]	H—$\overset{\vert}{\underset{\vert}{\mathrm{C}}}\mathrm{CH}_3$	167	4
IIIc[d]	H—$\overset{\vert}{\underset{\vert}{\mathrm{C}}}\mathrm{CH}_3$	232	4
IIIa	H—$\overset{\vert}{\underset{\vert}{\mathrm{C}}}\mathrm{CN}$	302	. . .

[a] See ref. 8. [b] Head-to-head polymer. [c] Estimated (see Experimental). [d] Head-to-tail polymer.

The polymer corresponding to IIIc was independently synthesized by a 1,6-elimination of hydrogen chloride from α-cyano-α-phenyl-α'-methyl-α'-chloroxylene using methanolic potassium hydroxide. Although this polymerization can conceivably proceed by a polycondensation mechanism involving displacement of the chloride ion by a carbanion, it is believed to proceed through a xylylene intermediate II. Such an elimination is novel as one would normally expect an α-chloroethylbenzene derivative to undergo 1,2-elimination to produce the corresponding styrene. The postulated xylylene intermediate II is supported by the speed of the reaction at room temperature, the production of relatively high molecular weight polymer in the presence of less than stoichiometric amounts of base, and by analogy with similar reactions which were shown to proceed through a xylylene intermediate.[13] The structure of this polymer, formed by reaction path $_3$, was shown to be head to tail by the n.m.r. data. The high softening point of this polymer and the presence of methyl groups (by infrared) in this polymer are in agreement with structure IIIc and support the structural assignment made for the equilibration polymer.

In contrast to the *para* isomer, the attempted equilibration of (*m*-vinylphenyl)phenylacetonitrile (V), a styrene which cannot form a relatively stable xylylene, resulted in polymer which by n.m.r. spectroscopy was found to contain only the structure VI (the *meta* equivalent of IIIb) and a small amount of vinyl and acetonitrile protons (polymer end groups). This polymer had no absorption near 7.25 μ and softened around 80°. The absence of methyl groups in this polymer indicates that the addition of a bulky anion

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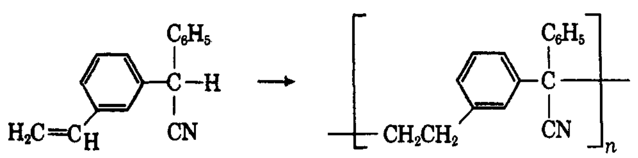

V VI

to styrene occurs only at the β-styrene position. Therefore the presence of methyl groups in the polymer from the p-styrene I must be due to the reaction of xylylene and not to the addition of the anion IV to the α-styrene position (route c_1).

Of the two remaining polymerization routes which can account for the structure IIIc in the polymer, the Michael addition (route c_2) appears to be more probable than the homopolymerization (route c_3). The ionization of the styrene I (R_1 = CN and R_2 = C_6H_5) to the anion IV was shown to be rapid and reversible. The formation of the anion can be noted visually by its red color and spectroscopically by its absorption at 485 mμ. Studies of proton exchange with deuterium showed that the acetonitrile proton is completely equilibrated in 1 N methanolic potassium hydroxide within 15 min. at room temperature. On the other hand, after 16 hr. of equilibration in the presence of deuterium ions no evidence was obtained for the addition of deuterium to the vinyl group. (Under these conditions most of the starting styrene was recovered unpolymerized.) This indicates that the addition of a proton to the p-quinoid resonance form of IV to give the xylylene is a slow process and perhaps, due to rapid reaction of the xylylene, not reversible. Because of its slow rate of formation and high reactivity the xylylene must be present in solution in extremely low concentration. Under such conditions and in the presence of large amounts of the anion IV (or a polymeric material containing this anionic structure) the Michael addition of IV to II (route c_2) appears to be the more probable reaction course. The head-to-tail arrangement of the structure IIIc in the polymer is in accord with such a mechanism although it does not rule out the homopolymerization (route c_3).

The present experiments demonstrate the presence of an equilibrium between a styrene and a xylylene but they do not measure the equilibrium constant. The ratio of IIIb to IIIc observed in the polymer is kinetically controlled and only indirectly dependent on the equilibrium concentration of the xylylene. The large amount of IIIc observed can be rationalized on the grounds that the rate of addition of the anion IV to the styrene I is slow (possibly due to steric effects around the anion) and the rate of formation of the xylylene II is sufficiently favored (electronic effects) to account for the observed ratio.

An alternate system of interest is that of 9-vinylanthracene (resonance energy 5.75β) and 9,10-dihydro-9,10-dimethyleneanthracene (resonance energy 5.68-β).[3,14] The small difference in energy between these compounds should allow ready interconversion in a suitably substituted system. However, an initial attempt to synthesize 9-vinyl-10-cyanomethylanthracene was not successful.

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Synthesis of 2-Acetamido-2-deoxy-3-*O*-(β-D-galactopyranosyl)-α-D-galactose

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The synthesis of 3-O-β-galactosyl-N-acetylgalactosamine (V) is reported. It involves condensation of 2,3,4,6-tetra-O-acetyl-α-D-galactopyranosyl bromide (IX), either with benzyl 2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-galactopyranoside (II), or with compound VI. In the latter case advantage is taken of the differential reactivity of the hydroxyl groups in the galactopyranose ring.

The disaccharide 2-acetamido-2-deoxy-3-O-(β-D-galactopyranosyl)-α-D-galactose (V) was isolated from an acid hydrolysate of human blood group A substance.[1] It is also found in hydrolysates of blood group B, H, and Le^a substances[2] and forms an essential part of their antigenic determinants.[3] Recent studies have shown that this disaccharide is inherent in the structure of the brain gangliosides[4,5] in which it constitutes the terminal part of the molecule.[6,7] The chemical[8] and enzymatic[9,10] syntheses of the glucosamine analog of V, also occurring in the blood group substances, have recently been reported. The present' synthesis was undertaken in connection with a study on galactosamine-containing oligosaccharides of N-acylsphingosine.

Benzyl 2-acetamido-2-deoxy-α-D-galactopyranoside (I) was prepared from 2-acetamido-2-deoxy-α-D-galactose by treatment with a solution of gaseous hydrogen chloride in benzyl alcohol at 70°. Although the corresponding glucosamine derivative has been prepared at reflux temperature,[11] these conditions caused extensive decomposition here, and only a negligible yield of the desired glycoside could be isolated. The reaction at 70° was followed polarimetrically and a maximum rotation was obtained after 8–10 hr. The crude amorphous product, isolated by precipitation with ether, was probably contaminated with a little of the β-isomer

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