much of the original *t*-butyllithium remains and only exchanges slowly with the rest. The equilibrium distribution of the species must be quite asymmetric and biased toward undissociated *t*-butyllithium tetramers. The same situation was observed in benzene, the spectrum being identical within the limits of experimental error.

It can be confirmed by viscosity measurements in hexane that *t*-butyllithium does not exchange as completely with polyisoprenyllithium as does *sec*-butyllithium. The concentration range in this case is of course much lower. A drop in dilute solution viscosity (η_{sp}/C) to 70% of its original value is caused by adding a fourfold excess of *sec*-butyllithium to polyisoprenyllithium. The same decrease requires an eightfold excess of *t*-butyllithium. Once again the viscosity reaches its limiting value within the time required for measuring the flow (~10 min) and does not change thereafter. Since in the viscosity experiments the molecular weight of the polyisoprenyl chain was much greater than used in the nmr experiments and hence much greater than that of the butyl group, any mixing of the separate species must cause a drop in average molecular weight and hence in dilute solution viscosity.

Conclusions

Most of the systems studied, *i.e.*, those not involving *t*-butyllithium, show fast exchange in cyclopentane at room temperature. The time scale between intermolecular exchange events must be fractional seconds. Under polymerization conditions in aliphatic solvents, where initiation takes many minutes, one may presume that when initiator is still present, a moving equilibrium distribution of alkyl and alkenyl species should be maintained. The exception seems to be the *t*-butyl containing systems, where complete intermolecular exchange takes many hours in mixing with either lithiomethyltrimethylsilane or *sec*-butyllithium. The alkenyl/*t*-butyl system behaves somewhat differently for an asymmetric equilibrium distribution is formed within the few minutes required for mixing and examination. It was suggested by Brown that the slow exchange of *t*-butyl-containing systems was determined by a slow dissociation rate of *t*-butyllithium aggregates. This explanation could be valid for the mixtures with *sec*-butyllithium and lithiotrimethylsilane where mixing seems to require approximately the same period of several hours. It cannot hold, however, for the *t*-butyllithium/polyisoprenyllithium system, since the dissociation hypothesis would require equilibration again to require several hours, whereas the time scale is no greater than minutes. It would seem that a different intermolecular exchange process occurs when polymer species are involved which might involve direct attack as previously suggested.[5] There is no doubt that exchange with *t*-butyl-containing species is slower than with either *n*-, *sec*-butyl or silyl compounds and mixing is less random when it occurs. This suggests that under some conditions use of *t*-butyllithium as a polymerization initiator could lead to different kinetic behavior than has been observed previously with the other initiators. This phenomenon has in fact been observed both in the polymerization of styrene and isoprene.[10]

Acknowledgment. The authors would like to thank Dr. J. E. L. Roovers for carrying out the viscosity measurements described above, and to Dr. S. K. Brownstein for advice and criticism.

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(10) J. E. L. Roovers and S. Bywater, unpublished observations.

Polymerization of α-*n*-Alkylstyrenes. I. Preparation of the α-*n*-Alkylstyrenes

H. Gisser and H. E. Mertwoy

Pitman-Dunn Research Laboratories, Philadelphia, Pennsylvania 19137.

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ABSTRACT: The Wittig reaction was used to prepare a series of new, pure, isomer-free α-*n*-alkylstyrenes. α-Pentyl-, α-heptyl-, α-nonyl-, α-undecyl-, α-tridecyl-, α-pentadecyl-, and α-heptadecylstyrene were prepared in 50–68% yields. To date, no pure, isomer-free α-*n*-alkylstyrene (alkyl > C_2H_5) has been reported. The identity of the new compounds was established by infrared spectroscopy and elemental analysis, and their homogeneity was proven by gas–liquid partition chromatography. As a preliminary experiment, the homopolymerization behavior of α-heptylstyrene and α-nonylstyrene were studied using sodium naphthalene as the catalyst at $-75°$. Both compounds formed low molecular weight polymers after 72 hr. The experimental evidence indicates that if an α-*n*-alkylstyrene is devoid of isomers, steric hindrance will not prevent homopolymerization.

In the course of the study on polymers having long alkyl chains, experiments were undertaken on the preparation of α-alkylstyrenes and steric and alkyl group length effects on polymerization. Aside from α-methylstyrene, there is very little information in the literature concerning the preparation and polymerization of α-alkylstyrenes.

Overberger, *et al.*,[1] suggested that the reason α-ethylstyrene forms only dimers and trimers under the same conditions (cationic polymerization) that α-methylstyrene forms a high molecular weight polymer is steric factors associated with the ethyl group. The

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(1) C. G. Overberger, E. M. Pearce, and D. Tanner, *J. Amer. Chem. Soc.*, **80**, 1761 (1958).

α-ethylstyrene was prepared through the pyrolysis of the acetates of the appropriate primary alcohol which was prepared by the reduction of the corresponding acid. Overberger and Tanner[2] in an earlier paper had reported α-ethylstyrene and α-propylstyrene prepared by the above method and mentioned that the possibility of small amounts of isomers cannot be excluded.

More recent investigations on the polymerizations of 1,1-disubstituted ethylenes, where one of the substituents is an alkyl group and the other a nitrile or acrylate, indicate that steric hindrance by an α-alkyl group greater than methyl will not prevent homopolymerization if the monomer is pure. Therefore, the presence of impurities in α-ethylstyrene rather than steric factors may have accounted for the failure of homopolymerization of this compound. Sorenson and Campbell[3] state that the monomer purity is essential for the success of practically any polymerization and that the monomer should be purified to give a single gas chromatographic peak.

Bailey, *et al.*,[4] prepared a series of α-alkylacrylonitriles (alkyl = C_2H_5 to C_6H_{13}) by the pyrolysis of the acetates derived from the corresponding cyanohydrins. These monomers were polymerized by peroxide and the resulting polymers did not have extremely high molecular weights; however, this was the first report of a solid homopolymer for this series. The investigators concluded that failure to obtain a high molecular weight polymer was due to the fact that the steric effect of the α-alkyl group probably exaggerated the effect of isomeric impurities on polymerization.

More recently a series of α-alkylacrylic esters (alkyl = C_2H_5 to C_4H_9) were prepared[5] and homopolymerized anionically forming high molecular weight polymers. The monomers were prepared by a series of reactions yielding an unambiguous product. The monomers did not, however, polymerize using free radical initiators.

In view of the above mentioned work on 1,1-disubstituted ethylenes, it was considered likely that relatively pure isomer-free α-alkylstyrenes with fairly long α-alkyl groups would homopolymerize. If so, the effect of steric hindrance on polymerization rate could be determined.

It was, therefore, necessary to find a method of preparation which would yield a pure unambiguous product. The compounds chosen for study were α-pentyl-, α-heptyl, α-nonyl-, α-undecyl-, α-tridecyl-, α-pentadecyl-, and α-heptadecylstyrene. Of the α-alkylstyrenes in which the alkyl is pentyl or larger, only α-pentylstyrene[6] and α-decylstyrene[7] had been reported. The former was prepared, however, by the dehydration of 2-hydroxy-2-phenylheptane which also yields isomers, whereas the latter is reported to be an impure compound, the position of the double bond not having been ascertained.

The patent literature[8] reports the preparation of polymers from monomers which are 1,1-disubstituted ethylenes having the general formula $R_1R_2C{=}CH_2$ where "R_2 is an alkyl group such as methyl, ethyl, propyl, isopropyl, etc., but is preferably methyl." The patent describes the polymerization of α-methylstyrene and does not give a method for the preparation of any of the monomers. There is no indication that any of the higher α-alkylstyrenes were either prepared or polymerized.

Search of the literature indicated that no pure, isomer-free α-*n*-alkylstyrene (alkyl > C_2H_5) has been prepared. Including the methods already mentioned, most preparations of α-alkylstyrenes yielded products containing isomers either due to rearrangement of the carbon skeleton or double bond isomerization. These methods consisted of dehydration[9] of the appropriate alcohol or dehydrohalogenation[10] of the appropriate alkyl halides. Reported decarboxylations of β-alkylcinnamic acids[11] were unsatisfactory due to low yields (18% for α-ethylstyrene).

Hughes,[12] however, was able to prepare isomer-free 4-methyl-2-phenylpentene-1 (58% yield) from methylenetriphenylphosphine and isovalerophenone using a method described by Wittig and Schöllkopf[13] for preparing olefins with unambiguous structures. The method is commonly known as the Wittig reaction. The compound was shown to be pure by gas–liquid partition chromatography. (Wittig and Schöllkopf[13] had prepared α-methylstyrene (74% yield) by this method.)

Corey and Durst[14] have prepared in high yields (76–99%) olefins, such as styrene and α-phenylstyrene, from the appropriate aldehyde or ketone and the lithio derivative of N-methanesulfinyl-*p*-toluidine and recently[15,16] reported the last step of the synthesis to be analogous to the mechanism of the Wittig reaction. However, no reactions were mentioned with *n*-alkylphenones to form α-*n*-alkylstyrenes, and, for the compounds prepared, no gas chromatographic analyses showing the absence of isomers in the olefins were reported.

In view of Hughes' work, the Wittig reaction appeared to be the best method for obtaining pure, isomer-free compounds and was, therefore, used for the preparation of the α-alkylstyrene. This method combined the extension of the carbon skeleton with the feature of position-specific introduction of the ethylenic group.

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(2) C. G. Overberger and D. Tanner, *J. Amer. Chem. Soc.*, **77**, 369 (1955).

(3) W. R. Sorenson and J. W. Campbell, "Preparative Methods of Polymer Chemistry," Interscience Publishers, New York, N. Y., 1961, p 6.

(4) W. J. Bailey, F. E. Naylor, and J. J. Hewitt, *J. Org. Chem.*, **22**, 1076 (1957).

(5) K. Chikanishi and T. Tsurruta, *Makromol. Chem.*, **74**, 198 (1965).

(6) F. Asinger, G. Geiseler, and W. Beetz, *Chem. Ber.*, **92**, 755 (1959).

(7) H. Gilman and R. N. Meals, *J. Org. Chem.*, **8**, 126 (1943).

(8) G. F. Hardy, U. S. Patent 3,169,948 (1965).

(9) (a) S. Sabetay, *Bull. Soc. Chim. Fr.*, **47**, 614 (1930); (b) P. Ramart-Lucas and P. Amagat, *C. R. Acad. Sci., Paris*, **184**, 30 (1927); (c) P. Ramart-Lucas and P. Amagat, *Ann. Chim.*, **8**, 263 (1927); (d) P. Ramart-Lucas and P. Amagat, *Bull. Soc. Chim. Fr.*, **51**, 108 (1932).

(10) (a) A. Klages, *Chem. Ber.*, **36**, 3688 (1903); (b) C. R. Hauser, P. S. Skell, R. D. Bright, and W. B. Renfrow, *J. Amer. Chem. Soc.*, **69**, 589 (1947).

(11) (a) J. D. A. Johnson and G. A. R. Kon, *J. Chem. Soc.*, 2748 (1926); (b) M. Tiffeneau, *Ann. Chim. Phys.*, **10**, 322 (1907).

(12) G. M. Hughes, *J. Chem. Soc.*, 3703 (1958).

(13) G. Wittig and U. Schöllkopf, *Chem. Ber.*, **87**, 1318 (1954).

(14) E. J. Corey and T. Durst, *J. Amer. Chem. Soc.*, **88**, 5656 (1966).

(15) E. J. Corey and T. Durst, *ibid.*, **90**, 5548 (1968).

(16) E. J. Corey and T. Durst, *ibid.*, **90**, 5553 (1968).

Another desirable feature of this reaction was the fact that it was essentially a one-step reaction. None of the intermediates had to be isolated, including methylenetriphenylphosphine prepared from methyltriphenylphosphonium bromide and *n*-butyllithium. Furthermore, methyltriphenylphosphonium bromide, *n*-butyllithium, and many of the ketones were commercially available. The rest of the ketones were made by facile, standard methods found in the literature.

Results and Discussion

Infrared spectroscopy and elemental analyses were employed to establish the identity of the α-alkylstyrenes, and gas–liquid partition chromatography established their homogeneity. Original yields obtained were as high as 80%, but since initial gas chromatographic analysis showed 0.07–3.0% ketone impurities, the compounds in petroleum ether (bp 30–75°) were percolated a second time through activated alumina and redistilled to remove the last traces of ketone, thus reducing the yields to a range of 50–60%.

In order to obtain some idea of the reactivity of the α-alkylstyrenes, preliminary polymerization experiments were carried out with α-heptylstyrene and α-nonylstyrene using sodium naphthalene (radical-anion initiator) as the catalyst.[17] With α-heptylstyrene and α-nonylstyrene, the red color of the dianion was very slow to develop and did not persist for more than a few minutes. It was, therefore, necessary to add small increments of catalyst to the solution of monomer in tetrahydrofuran at −75° over a period of several hours until the red color did persist. In contrast, the initiation of the polymerization of α-methylstyrene in tetrahydrofuran at −75° (run as a control) was very rapid; the red color of the dianion formed immediately. The polymerization of α-methylstyrene was terminated by the addition of methanol after 5 hr yielding poly(α-methylstyrene) having a high molecular weight as expected. Because of the difficulty in initiating the polymerization of α-heptylstyrene and α-nonylstyrene, it seemed plausible that the polymerization rate might be a good deal slower than that of the α-methylstyrene dianion. Therefore, the polymerizations were allowed to continue for 72 hr before the dianions were destroyed. Polymeric products of both α-heptylstyrene and α-nonylstyrene were isolated in small yield. Approximately 85% of the monomer was recovered in both cases.

The infrared spectra of both polymeric substances indicated them to be poly(α-heptylstyrene) and poly(α-nonylstyrene) by the absence of such characteristic olefinic bands at 1799 and 892 ($RR'C{=}CH_2$)[18] and 1630 cm^{-1} ($C_6H_5C{=}C$)[19] and the presence of only CH_2, CH_3, and phenyl bands. The spectra of these two compounds were very similar to that of polystyrene and poly(α-methylstyrene) with the exception of a shoulder at 720 cm^{-1} [20] indicating the presence of $-(CH_2)_n-$ where $n \geqq 4$, in this case heptyl or nonyl.

The average molecular weight determined by vapor pressure osmometry indicated that the polymeric substance from the α-heptylstyrene reaction contained, on an average, more than six units of monomer, and the polymeric substance from the α-nonylstyrene reaction contained, on an average, between five and six units of monomer. It may be noted that Chikanishi, *et al.*,[5] using the same polymerization technique (sodium naphthalene as the catalyst), converted 90.9% of isomer-free methyl α-ethylacrylate to a high molecular weight polymer in 3 days, but only 75.7% of isomer free methyl α-butylacrylate was converted to a high molecular weight polymer after 7 days. Furthermore, it has been found in this laboratory[21] that isomer-free methyl α-dodecylacrylate under the same conditions forms a low molecular weight polymer after 24 hr and a high molecular weight polymer after 3 weeks. From the foregoing, it seems a reasonable hypothesis that if an α-alkylacrylate or styrene is relatively pure and isomer free, homopolymerization may be experimentally achieved although the rate may be considerably reduced by steric effects.

This is a preliminary report and is the first report of homopolymers from α-alkylstyrenes with the alkyl group larger than methyl. Although the molecular weights of the polymers of α-heptyl- and α-nonylstyrene were not high, it is expected that, if the reaction time of the polymerization were extended from 72 hr to possibly several weeks, high molecular weight polymers would have been obtained. A more detailed investigation of the effect of chain length of the α-alkyl group and reaction time on the polymerizations of α-alkylstyrene is in progress and will be reported in a future paper.

Experimental Section[22]

α-Pentylstyrene (I). Methyltriphenylphosphonium bromide (0.082 mol) was added in small portions to a stirred solution of butyllithium (52 ml of a 1.6 *M* hexane solution of butyllithium in 100 ml of anhydrous ethyl ether) under nitrogen during 1 hr. Maintaining a nitrogen atmosphere, hexanophenone (0.082 mol) dissolved in 100 ml of anhydrous ethyl ether was added to the resulting red solution of methylenetriphenylphosphine over a 1-hr period. The solution was refluxed for 3 hr and stirred overnight at room temperature. The residue, triphenylphosphine oxide, was filtered off and washed with ether, and the combined filtrates were washed with water and dried over anhydrous sodium sulfate. After filtering off the sodium sulfate, the solvents were removed under reduced pressure. The remaining α-pentylstyrene dissolved in petroleum ether (bp 30–75°) was percolated twice through columns of activated alumina to remove unreacted ketone and traces of triphenylphosphine oxide. The olefin was further purified by fractionating (Vigreux column) *in vacuo* giving a 52% yield, distillation temperature 57° (0.9 mm), n^{25}D 1.50967. The olefin was shown to be homogeneous by gas–liquid partition chromatography.

Anal. Calcd for $C_{13}H_{18}$: C, 89.58; H, 10.42. Found: C, 89.81; H, 10.50.

α-Heptylstyrene (II). This was prepared in the same

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(17) M. Szwarc, M. Levy, and R. Milkovich, *J. Amer. Chem. Soc.*, 78, 2656 (1956).

(18) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, N. Y., 1960, p 34.

(19) See ref 18, p 41.

(20) See ref 18, p 27.

(21) H. Gisser and H. E. Mertwoy, unpublished work.

(22) Microanalyses were performed either by this laboratory or Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Infrared spectra were obtained employing a Perkin-Elmer Model 21 spectrophotometer. Gas chromatograms were determined on a Hewlett-Packard 5750 research chromatograph using a silicone gum rubber column at 150°.

manner as α-pentylstyrene (I) using octanophenone (0.082 mol). A 65% yield was obtained, distillation temperature 84° (0.15 mm), $n^{25}\text{D}$ 1.50432. The olefin was shown to be pure by gas–liquid partition chromatography.

Anal. Calcd for $C_{15}H_{22}$: C, 89.04; H, 10.96. Found: C, 88.85; H, 10.91.

α-Nonylstyrene (III). This was prepared in the same manner as α-pentylstyrene (I) using decanophenone (0.082 mol). A 57% yield was obtained, distillation temperature 106° (0.25 mm), $n^{25}\text{D}$ 1.49957. Gas–liquid partition chromatography proved the compound to be homogeneous.

Anal. Calcd for $C_{17}H_{26}$: C, 88.62; H, 11.38. Found: C, 88.75; H, 11.66.

α-Undecylstyrene (IV). This was prepared in the same manner as α-pentylstyrene (I) with two exceptions. The ketone, dodecanophenone (0.082 mol), was not as soluble as the lower molecular weight ketones in ether so that it was necessary to use 200 ml of anhydrous ethyl ether to dissolve it. After the ketone was added (a 1-hr addition time still being used), the reflux time was increased from 3 to 4 hr. A 50% yield was obtained, distillation temperature 137° (0.50 mm), $n^{25}\text{D}$ 1.49607, gas–liquid partition chromatography proved the compound to be homogeneous.

Anal. Calcd for $C_{19}H_{30}$: C, 88.30; H, 11.70. Found: C, 88.02; H, 11.65.

α-Tridecylstyrene (V). This was prepared in the same manner as α-pentylstyrene (I). However, as with compound IV, it took 200 ml of anhydrous ether to dissolve the ketone, tetradecanophenone[23] (0.082 mol). After the addition of the ketone, a 5-hr reflux period was employed. A 68% yield was obtained, distillation temperature 141° (0.14 mm), $n^{25}\text{D}$ 1.49367. Gas–liquid partition chromatography proved the compound to be homogeneous.

Anal. Calcd for $C_{21}H_{34}$: C, 88.02; H, 11.98. Found: C, 87.95; H, 12.00.

α-Pentadecylstyrene (VI). This was prepared in the same manner as α-pentylstyrene (I). However, as with compound IV, it took 200 ml of anhydrous ether to dissolve the ketone, hexadecanophenone[23] (0.082 mol). After the addition of the ketone, a 4-hr reflux period was employed resulting in a 50% yield, distillation temperature 183° (0.62 mm), $n^{25}\text{D}$ 1.49210. With the longer chain alkylphenones, it is possible that higher yields could be obtained with a longer reflux period. The olefin was proven to be homogeneous through gas–liquid partition chromatography.

Anal. Calcd for $C_{23}H_{38}$: C, 87.82; H, 12.18. Found: C, 88.18; H, 12.56.

α-Heptadecylstyrene (VII). This was prepared in the same manner as α-pentylstyrene (I). The ketone, octadecanophenone[23,24] (0.082 mol), was even less soluble in ether than the ketones used to prepare compounds IV, V, and VI. It required 250 ml of anhydrous ethyl ether to dissolve the ketone, and a 7-hr reflux period was used. A 51% yield was obtained, distillation temperature 162° (0.08 mm). All the other styrenes prepared were liquids; however, this compound solidified on standing at room temperature, indicating that its melting point is very close to 25°. Gas–liquid partition chromatography proved the compound to be homogeneous.

Anal. Calcd for $C_{25}H_{42}$: C, 87.64; H, 12.36. Found: C, 87.45; H, 12.51.

Infrared Spectra of the α-Alkylstyrenes. Since all the compounds were liquids (α-heptadecylstyrene being a low melting solid), the infrared spectra were obtained neat. All the α-alkylstyrenes showed absorption bands in the regions characteristic for compounds having the structure $RR'C{=}CH_2$ where R is an *n*-alkyl group and R′ is a phenyl group. The bands are as follows: 1630 ($C_6H_5C{=}C$),[19] 1799 and 892 ($RR'C{=}CH_2$),[18] 776 and 690 (C_6H_5),[25] and a shoulder at 720 cm^{-1} ($-(CH_2)_n-$ where $n \geqq 4$).[20]

Polymerization Reactions. A. Purification of Nitrogen. Because of the extreme sensitivity of both the catalyst (sodium naphthalene) and the dianions to moisture and oxygen, all reactions and distillations were carried out in a pure nitrogen atmosphere. The nitrogen (containing 8 ppm oxygen) was purified passing it through a tube of copper gauze heated to 500° and then through a molecular sieve connected to a moisture indicator.

B. Purification of Monomers. Monomers were stored in a desiccator (at 8°) and redistilled *in vacuo* under nitrogen (into a receiving flask with a side arm closed by a septum) before polymerizations.

C. Purification of Tetrahydrofuran. The solvent was purified by distilling twice over sodium metal in a nitrogen atmosphere. The distillate was collected in a receiver with a side arm closed by a septum.

D. Preparation of Sodium Naphthalene. The initiator was prepared by a method similar to that described for lithium naphthalene.[26] Sodium (0.11 mol) and naphthalene (0.11 mol) in 30 ml of tetrahydrofuran were stirred overnight under nitrogen resulting in a dark green solution of sodium naphthalene complex. The reaction flask also had a side arm closed by a septum.

E. Polymerization of α-Heptylstyrene. The monomer was polymerized by a method similar to that described for α-methylstyrene.[26] The reaction flask had a side arm closed by a septum through which the reactants could be injected. A solution of 13 g of styrene in 50 ml of tetrahydrofuran was cooled to −75° in a nitrogen atmosphere. While stirring, small increments of sodium naphthalene were injected through the septum into the reaction flask, till the solution assumed the reddish color of a styrene dianion. Unlike α-methylstyrene,[27] which assumed the red color of the dianion immediately, it took 3 hr to initiate the polymerization of α-heptylstyrene. The polymerization was allowed to continue for 72 hr and then terminated with methanol. After warming to room temperature, an excess of methanol was added to the reaction mixture. The polymer settled out, and the solvents were decanted. From the solvents, approximately 85% of α-heptylstyrene was recovered. The polymer was washed with methanol several times, and the methanol decanted. The product was dissolved in warm toluene, and the solution allowed to cool to room temperature. It was then filtered, and the filtrate washed with water (to remove the alkali) till neutral. After drying over anhydrous sodium sulfate and filtering off the sodium sulfate, methanol was added to the toluene solution till it became milky white. The solution was allowed to stand overnight, after which time the polymer had settled to the bottom of the flask. The clear supernatant liquid was decanted, and the product washed several times with methanol which was decanted. The polymer was dried in a vacuum oven yielding a tacky, clear solid. The infrared spectrum showed only the presence of CH_2, CH_3, and phenyl

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[23] Prepared by a method described by F. L. Breusch and M. Oguzer, *Chem. Ber.*, **87**, 1225 (1954).

[24] Preparation of stearoyl chloride, used to prepare the ketone, is described by S. T. Bauer, *Oil Soap*, **23**, 1 (1946).

[25] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, N. Y. 1960, p 65.

[26] W. R. Sorenson and T. W. Campbell, "Preparative Methods of Polymer Chemistry," Interscience Publishers, New York, N. Y., 1961, p 198.

[27] To ensure that optimum conditions existed for a radical-anion polymerization, α-methylstyrene was polymerized as a control. As expected, it polymerized readily to a high molecular weight solid in 5 hr using the method described by Sorenson and Campbell.[26]

bands; the olefin bands at 1799 and 892 ($RR'C{=}CH_2$) and 1630 cm^{-1} ($C_6H_5C{=}C$) had disappeared. The average molecular weight of the product, determined by vapor pressure osmometry, was 1219. This corresponded to a little more than six units of monomer (molecular weight of α-heptylstyrene is 202).

F. Polymerization of α-Nonylstyrene. This compound was polymerized in a manner identical with that of α-heptylstyrene, the initiation and reaction times being the same. In this case, however, 8.5 g of monomer dissolved in 50 ml of tetrahydrofuran was used. The infrared spectrum was very similar to that of the polymerized α-heptylstyrene. All the olefin bands were missing. The average molecular weight, determined by vapor pressure osmometry, was 1202 which corresponds to 5.2 units of monomer (molecular weight of α-nonylstyrene is 230).

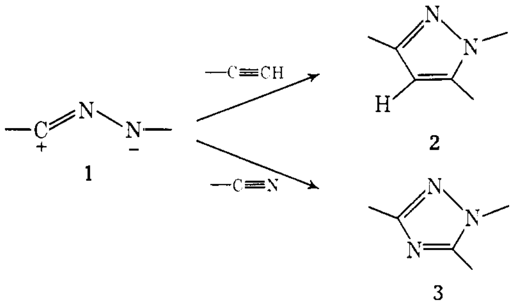
1,3-Dipolar Addition Polymerizations. The Synthesis and 1,3-Dipolar Addition Polymerization of Dipole–Dipolarophile (A–B) Monomers Containing Tetrazole and Vinyl or Ethynyl Moieties

J. K. Stille and L. D. Gotter[1]

Department of Chemistry, University of Iowa, Iowa City, Iowa 52240. *Received May 26, 1969*

ABSTRACT: The syntheses of two new A–B monomers containing a tetrazole moiety connected by a *p*-phenylene bridge to a vinyl or ethynyl group has been carried out. The 1,3-dipolar homopolymerization of the two A–B monomers yielded poly(1-phenyl-3-*p*-phenylene-Δ^2-pyrazoline) (**11**) and poly(1-phenyl-3-*p*-phenylenepyrazole) (**12**). The polymers possessed intrinsic viscosities of 0.58 and 0.75 and were stable in air to 360 and 460°, respectively. The polymers were soluble in polar and acidic solvents.

A number of 1,3-dipolar cycloaddition reactions have been employed for the formation of five-membered heterocycles; the mechanistic and kinetic aspects of many of these reactions are now reasonably well established.[2] The products of the 1,3-dipolar cycloaddition of nitrilimines (**1**) to acetylenes and nitriles are pyrazoles (**2**) and triazoles (**3**). The 1,3-dipolar cycloaddition reaction of nitrilimines is a useful polymer-forming reaction since the reactions often proceed in high yield, and the product linkages (**2, 3**) contain an aromatic sextet desirable for good thermal stability. Suitable nitrilimine dipoles may be generated either by treating hydrazide chlorides, in solution, with a base such as triethylamine, or by the pyrolysis of 2,5-disubstituted tetrazoles.[2] Polymerization studies carried out in this laboratory with bishydrazide chlorides and bistetrazoles have shown the tetrazole ring to be a superior nitrilimine precursor with respect to polymer yield and molecular weight.[3-5] A polypyrazole having an intrinsic viscosity of 1.67 (0.300 g/100 ml of 98% formic acid at 30°) and a thermal stability in air to nearly 500° has been obtained[5] from the reaction of a bistetrazole with a diethynyl compound. Although thermally stable polymers of moderate molecular weight could be synthesized using bistetrazoles as nitrilimine precursors, the syntheses of A–B monomers containing both the dipole and the dipolarophile were desirable.



Discussion

Monomer Syntheses. In choosing a synthetic pathway for 2-phenyl-5-(4′-vinyl)phenyltetrazole (**4**) and 2-phenyl-5-(4′-ethynyl)phenyltetrazole (**5**) (Scheme I), consideration was given to the relative reactivities of the functional groups present (tetrazole and vinyl or ethynyl) in the two A–B monomers. The tetrazole ring was synthesized first for several reasons: first, the aldehyde precursor of the tetrazole ring is unstable to the conditions required to generate a vinyl or ethynyl group, and second, the vinyl and ethynyl groups could be expected to decompose partially during the synthesis of the tetrazole if they were already present in the system. In addition, the tetrazole ring is relatively stable to the reagents required for the synthesis of the vinyl or ethynyl groups. Reaction of the phenylhydrazone of *p*-tolualdehyde (**6**), with phenyl azide in 2-methoxyethanol containing sodium 2-methoxyethoxide, afforded 2-phenyl-5-(4′-methyl)phenyltetrazole (**7**) in

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(1) Lubrizol Fellow, 1968–1969.

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