Several experiments were performed to examine the use of lithium dimethylamide as a base for generating lithium enolate anions. The following procedure is illustrative. The ether was removed from 1 ml. of an approximately 1 *M* ethereal solution of methyllithium under reduced pressure and the residual lithium reagent, under a nitrogen atmosphere, was treated with 1.4 ml. of 1,2-dimethoxyethane containing 1.33 mmoles of dimethylamine. In other comparable experiments, it was shown that 1 mole of methane is rapidly evolved for each mole of methyllithium employed. Several milligrams of triphenylmethane (as an indicator) was added to the solution of lithium dimethylamide²³ and 2-

(23) Other experiments performed by Mr. Ben Tefertiller in our laboratories have demonstrated that lithium dimethylamide attacks the solvent, 1,2-dimethoxyethane, relatively rapidly **so** that it is not practical to store these solutions for more than 1 hr. Thus, these solutions are distinctly less stable than solutions of triphenylmethylpotassium.¹⁶

methylcyclopentanone (105.4 mg. or 1.08 mmoles) **was** added until the red color of the triphenylmethyl anion was discharged. The resulting solution was concentrated under reduced pressure to remove dimethylamine and then diluted with 1 ml. of 1,2 dimethoxyethane; the concentration and dilution process was then repeated. At this time no dimethylamine could be detected (moist litmus paper) in a stream of nitrogen which had been passed through the solution. The solution was then added to 2.26 g. (22.2 mmoles) of acetic anhydride and the enol acetates were isolated from the mixture and analyzed in the usual way. The composition of the enol acetate mixture was 30% enol acetate **5** and 70% enol acetate **6** with the calculated yields being 28% of 1, 12% of 5, and 29% of 6. Comparable yields and enol acetate compositions were obtained in two additional experiments. Thus, the conditions employed correspond to kinetically controlled enolate formation with triphenylmethyllithium.

Electrolytic Reductive Coupling. VI.¹ Aromatically Substituted Ethylenes²

MANUEL M. BAIZER AND JAMES D. ANDERSON

Central Research Department, Mmsanto Company, St. Louis, Missouri 63166

Received November 13, 1964

Illustrative examples (9-benzalfluorene and 2-phenyl-1,3-butadiene) are presented of the hydrodimerization of highly conjugated olefins upon electrolysis in relatively concentrated solution in quaternary ammonium electrolytes. When the ethylenic hydrogens are substituted by bulky groups, reduction occurs but hydrodimerization is blocked If the hydrocarbons are electrochemically reduced at a cathode voltage more positive than that of a given Michael acceptor, they may be reductively coupled with the acceptor. Thus 9-benzalfluorene couples with 1 mole of ethyl acrylate and with 2 moles of acrylonitrile; **8,8-diphenylbenzofulvene** couples with 3 moles of acrylonitrile.

The polarographic reduction of conjugated olefins and the elucidation of the mechanism of the electrode process have been the subjects of extended studies. $3,4$ When there is no intervention of proton donors, two rapid successive one-electron additions are indicated leading from the hydrocarbon (I) through the anion-

free radical (II) to the dianion (III). The over-all
\n
$$
RCH=CHR' \xrightarrow{\mathbf{e}} RCH-CHR' \xrightarrow{\mathbf{e}} RCH-CHR'
$$
\n
$$
H \xrightarrow{\mathbf{f}} H \xrightarrow{\mathbf{f}} H
$$

effect is a two-electron uptake. When the intermediate I1 can react with a proton at the electrode surface,

the sequence of events is modified as follows. The
\n
$$
I + e \overline{\smash{\bigstar}} II + H^+ \longrightarrow RCH - CH_2R' + e \longrightarrow R - CH - CHR' + H^+
$$
\n
$$
R - CH - CHR' + H^+
$$
\n
$$
RCH_2CH_2R'
$$

formation of reduced dimers electrochemically has been ascribed in the case of stilbene³ ($R = R' = C_6H_5$) to the coupling of two radicals (11) followed by the reaction of the dianion IV with water or other proton

$$
2RCH-CHR' \longrightarrow R'CH-CH-CH-CHR' \xrightarrow{2H_1O} R'R
$$

\n
$$
R'R
$$

\n
$$
R'CH_2-CH-CH_2R' + 2OH^-
$$

(1) Paper V: J. D. Anderson, M. M. Baiaer, and E. J. Prill. *J. Ow. Chem., SO,* 1645 (1965).

donor. It is considered that under polarographic conditions a dianion I11 reacts with water to form the dihydro compound, 5 whereas in the reduction of conjugated hydrocarbons (I) with sodium the intermediate I11 adds to another molecule of I to produce reduced $dimer⁶$ Reduction of stilbene in the presence of carbon dioxide has been reported to yield meso-diphenylsuccinic acid presumably by stepwise addition of electrons and carbon dioxide.³

As part of our program on electrolytic reductive coupling of activated olefins in relatively concentrated aqueous solution,^{7} we examined the behavior of 9benzalfluorene, 2-phenyl-1,3-butadiene, and 8,8-diphenylbenxofulvene in hydrodimeriaations and of the pairs **9-benealfluorene-acrylonitrile,** 8,8-diphenylbenzofulvene-acrylonitrile, and 9-benzalfluorene-ethyl acrylate in mixed reductive couplings. In the absence of mechanistic studies we have scrutinized the results for consistency with the proposal that carbanionic intermediates are involved.

Hydrodimerizations.—It is known that 9-benzalfluorene is a Michael acceptor.⁸ Electrolysis of a solution of this hydrocarbon in aqueous methyltrin-butylammonium p-toluenesulfonate containing dimethylformamide was carried to only partial conversion. **A** 66% yield (based on current) of the known hydro dimer **1,2-dipheny1-1,2-bis(9-fluorenyl)ethane** was obtained. During the reaction the surface of the mercury cathode was red.3

2-Phenyl-l,3-butadiene in a similar experiment gave the known dihydro compound 2-phenyl-2-butene (V)

- **(6)** K. Ziegler, H. Colonius, and 0. Schafer. *Ann.,* **478,** *36* (1929).
- (7) M. M. Baiaer, Tetrahedron *Leftera,* 973 (1963).

⁽²⁾ Presented at the 148th National Meeting of the American Chemical

Society, Chicago, Ill., Sept. 1964; Abstracts, p. 75S.
(3) S. Wawzonek, E. W. Blaha, R. Berkey, and M. E. Runner, *J. Electro-*

chem. Soc., 102, 235 (1955), and references cited therein.
(4) G. J. Hoijtink, *Rec. trav. chim.*, 76, 885 (1957), and references cited therein: T. J. Kata, *et* **al..** *J. Am. Chem. Soc.,* **84,** *802* (1962).

⁽⁵⁾ I. M. Kolthoff and J. J. Lingane, "Polarography," **1'01.** *2,* 2nd Ed., Interscience Publishers, Inc., New York, N. Y.. 1952, p. 641 8.

⁽⁸⁾ E. Bergmann, D. Ginsburg, and R. Pappo, *Ow.* Reactions, **10,** 179 (1959).

in the amount equivalent to *85%* of the current input, the hydro dimer **VI** in 8.3% yield (same basis), and the known Diels-Alder dimer⁹ VII (which arose independently of the electrolysis).

An attempted hydrodimerization of 8,8-diphenylbenzofulvene failed. Reduction occurred readily, the surface of the mercury turned green, but apparently only the dihydro product was formed.1° This is an excellent example of a case in which electronic factors favor carbanion formation but steric factors prevent addition of the carbanion to a bulky acceptor. In similar circumstances sodium also fails to effect reductive dimerization of conjugated olefins.^{11,12}

Mixed Reductive Couplings.--During electrolysis of a mixture of 9-benzalfluorene and acrylonitrile $(1:10)$ molar ratio) in a similar electrolyte no red coloration was observed at the cathode, indicating that the postulated intermediate carbanion reacted extremely rapidly

(9) C. 9. Marvel and E. J. Call, *J. Ore. Chem.,* **44,** 1494 (19.59). (10) **The product** of **sodium reduction is reported" to be the following.**

(11) W. **Schlenk,** *el al., Ann.,* **468,** 63 (1928). (12) C. B. Wooster, Chem. Rev., 11, 1 (1932).

with the acceptor. No hydro dimers were found. The major product was a biscyanoethyl compound **XI11** ; a minor amount of 9-benzylfluorene **(X)** was formed as a by-product. (See Scheme **I.)**

While fluorene has been dicyanoethylated,¹³ 9-benzylfluorene failed to react with acrylonitrile under the usual Michael conditions.¹⁴ The above electrochemical reaction again¹⁵ illustrates the postulated formation of a carbanion **(IX)** which can not be formed by proton abstraction from the corresponding saturated compound.

The two electrons supplied at the cathode have been instrumental in causing the introduction of the first cyanoethyl group (at the benzylic position). Adduction of the second acrylonitrile molecule is a secondary consequence of the sequence of events initiated by the original reduction.

Reductive coupling of **8,8-diphenylbenzofulvene** with acrylonitrile was complicated by the fact that the hydrocarbon could not be brought into solution in the catholyte unless only a very low per cent of water was present. Polyacrylonitrile was formed" as well as a triscyanoethylated product **XIV.** The structure proposed is consistent with the n.m.r. spectrum and the data on the cyanoethylation of the indene system.^{13,18} The current input corresponded to a two-electron uptake. Bruson has reported¹³ the triscyanoethylation of indene itself but only monocyanoethylation of 8,8-dimethylbenzofulvene. (See Scheme **11.)**

Electrolysis of a mixture of 9-benzalfluorene and ethyl acrylate (1 : 10 molar ratio) yielded 9-benzylfluorene and a small quantity of the expected product of mixed reductive coupling **(XV).**

Experimental¹⁹

Apparatus and General Procedure.-These have been described previously.²⁰ A mercury cathode, area 55 cm.², was used **throughout. Traces of stabilizer were always added to the starting olefins and were replenished during subsequent handling.**

Electrolytic Hydrodimerization of 9-Benzalfluorene.-The catholyte contained 26.4 g. (0.104 mole) of 9-benzalfluorene,²¹ **58.9** g. **of dimethylformamide, and 59** g. **of 82.6% aqueous** methyltri-n-butylammonium **p-toluenesulfonate. The anolyte** was 20 g. of a 47% solution of the same quaternary salt. An **average of 2.0 amp. was passed in at** 45° **for 1 hr. at a cathode voltage of** -1.5 **to** -1.6 **v. (s.c.e.).** The pH was moderated by

(13) **H. Bruson,** *J. Am. Chem. Soc..* **64,** 2457 (1942); *Oru. Reactiot's,* **6,** 107 (1949).

(14) N. **Campbell, et** *ol., J. Chem.* Soc., 1239 (1949).

(15) **Paper** IV: M. M. **Baiser,** *J. Ore. Chem.,* **49,** 1670 (1964).

(16) We may assume on the basis of **Campbell's work" that if** XI or XII **reacted first at C-9 with water the resulting products would have been incapable of reverting to the carbanions in the mildly alkaline aqueous environment. This is borne out by the fact that** X **was isolated from the** reaction mixture even though a large excess of acrylonitrile was present.

(17) **The electrochemical anionic polymerization of acrylonitrile will be discussed in a future paper.**

(18) **H. Dressler and R.** J. **Kurland,** *ibid..* **48,** 175 (1964).

(19) **Boiling points are uncorrected. Mercury was used as a cathode throughout. When compounds previously reported in the literature were obtained here, their elemental and molecular weight analysea were checked and found to be satisfactory.**

(20) Paper I: **M.** M. **Baizer,** *J. Elecfrochem. SOC.,* **ill,** 215 (1964).

(21) *Y.* **Sprinzak,** *J. Am. Chem. Soc.. 78,* 466 (1956).

the addition of ca. 3 ml. of acetic acid in the course of the run. Product began precipitating after the first 30 min. At the end of the run the mercury was separated and the product (11.5 g) was removed by filtration and dried *in vacuo*, m.p. $310-313^{\circ}$. Reremoved by filtration and dried in vacuo, m.p. 310-313°. crystallization from anisole raised the melting point to 319-320" (lit.'' **m.p.** 321' for **1,2-diphenyl-1,2-bis(9-fluorenyl)ethane).** The original filtate was diluted with water and the precipitated solid was removed by filtration, dried, and extracted overnight in a Soxhlet with hexane. The insoluble portion (1.0 g.) was additional product.

Electrolysis of 2-Phenyl-1,3-butadiene.²²-The catholyte contained 66.6 g. of olefin, 73.5 g. of tetramethylammonium *p*toluenesulfonate, 4.9 g. water, and 114.5 g. of dimethylformamide. Electrolysis was conducted at 25° at an average of 2.0 amp., total 12.0 amp.-hr. The cathode voltage was -2.0 v. $(s.c.e.).$ The catholyte was diluted with 200 ml. of. water and extracted with five 50-ml. portions of cold methylene chloride in the presence of hydroquinone. The extracts were washed and dried over sodium sulfate. After the solvent was distilled from a water bath, the residual liquid was fractionated through a 3-ft Vigreux column to separate lower boiling components (A, 52.2) **g.)** from the higher boiling residue (B, 13.2 g.). Three successive fractions of A [total range from 45° (11 mm.) to 62° (5 mm.)] were analyzed by V.P.C. and found to contain dimethylformamide, 2-phenyl-l,3-butadiene, and increasing quantities of V which constituted 80% of the highest boiling fraction. The total quantity of V found in A was 22.7 g. Pure V, n^{25} D 1.5374, was collected during passage of the V-rich fraction through an F and M Model 770 automatic preparative gas chromatograph using a column of silicone grease on Chromasorb W at 125'.

The infrared spectrum was identical with that of authentic $cis-2$ -phenyl-2-butene. A solution of B in $ca. 2 g.$ of methylene chloride was filtered to remove a small quantity of hydroquinone. A sample of the filtrate was analyzed by V.P.C. and was found to contain 2.4 g. of additional V, 4.6 g. of VI, 3.7 g. of VII, $^{\circ}$ and four minor components. On chilling the methylene chloride solution crystals of VI separated which were removed by filtration and recrystallized from ethanol; m.p. 71.5-73°.

Anal. Calcd. for $C_{20}H_{22}$: C, 91.60; H, 8.40; mol. wt., 262. Found: C, 91.60; H, 8.49; mol. wt., 262 (mass spectrum).

The proton magnetic resonance spectrum was determined at room temperature on the Varian A-60 spectrometer. Carbon tetrachloride was used as the solvent and tetramethylsilane as internal standard. The spectrum of the sample was obtained in 20% solution by volume. The δ values and the intensities of the signals of the samples are listed below: a doublet at -1.64 (5.97H, methyl protons), a singlet at -2.51 (4.03H, methylene protons), a quartet at -5.63 (2.09H, olefinic protons), and a multiplet at -7.20 (10.00H for aromatic protons).

The infrared spectra (Nujol and carbon disulfide) had absorptions at 1640 and 833 cm.^{-1} characteristic of trisubstituted olefins.

CH₂CH₂CN then dried over Drierite. Volatile materials were removed on
 $-CH_2CH_2CN$ the water bath using an aspirator. The residual amber sirup

weighed 53.5 g.; the excess weight was due to quaternary am-

monium salt Electrolytic Reductive Coupling **of** 9-Benzalfluorene and Acrylonitrile.-The catholyte contained 19.6 g. (0.0773 mole) of benzalfluorene, 41.0 g. (0.773 mole) of acrylonitrile, 25 g. of dimethylformamide, and 65.9 g. of 83% aqueous methyltri-nbutylammonium p -toluenesulfonate. The anolyte was 20 g. of a 47% solution of the above salt. Electrolysis at 30° was done at a controlled cathode voltage of -1.51 to -1.60 v. (s.c.e.). The amperage decreased from 2.0 to 0.10 amp., total 3.67 amp.hr. The pH was kept at ca. 8 by gradual addition of 1.60 ml. of acetic acid. At the end of the run the mercury was separated and a small amount of solid was removed by filtration. After purification from hexane, it yielded 0.44 g. of 9-benzylfluorene, m.p. $134-135^{\circ}$ (lit.²¹ m.p. $134-135^{\circ}$). The original mother liquor was diluted with 200 ml. of water and extracted with four 50-ml. portions of methylene chloride. The extracts were washed and the water bath using an aspirator. The residual amber sirup weighed 53.5 g.; the excess weight was due to quaternary ammonium salt which had been extracted along with product. The sirup was washed by decantation first with water and then with ethanol. From a methanol solution of the insoluble portion there was obtained 0.9 g. and from the ethanol solution **0.7** g. of 9-benzylfluorene. The combined ethanol-methanol mother liquors were evaporated to dryness. The residue was dissolved in 200 ml. of methylene chloride and purified by passage through a column of activated alumina, which retained the quaternary salt impurity. The effluents yielded 21.4 g. (76.4% based on current input) of crude sirupy XIII. Trituration with ether caused crystallization. Recrystallization from methanol provided the white analytical sample, m.p. 126-127".

Anal. Calcd. for XIII, $C_{26}H_{22}N_2$: C, 86.15; H, 6.12; N, 7.73. Found: C, 85.66; H, 6.08; **N,** 7.95.

The proton magnetic resonance spectrum was determined under the conditions described above. The spectrum of an authentic sample of 9-benxylfluorene was used as a model compound. The proton of interest in this model compound is the proton attached to the 9-position of the fluorene nucleus $(\delta -4.2)$. This proton is clearly absent from the spectrum of the biscyanoethyl compound showing the structure to be XI11 and not the isomer shown below.

Preparation of 8,8-Diphenylbenzofulvene.-Sodium methoxide (1.0 mole), ethanol (1000 ml.), and benzophenone (1.0 mole) were charged to a 2-1. four-necked flask equipped with a reflux condenser, thermometer, Trubore stirrer, and dropping funnel. Indene (1.0 mole) was added dropwise at room temperature after which the reaction mixture was slowly warmed to reflux and then maintained at reflux for 5 hr. Concentrating and cooling the ethanolic solution gave two crops of bright yellow product.

⁽²²⁾ C. *C.* **Price,** *et* **al.,** *J. Am.* **Chem.** *Soc..* **71,** *2860* (1949)

After recrystallization from 2-propanol the product weighed 140 g. (50%) , m.p. 110-111° (lit.²³ m.p. 111°)

Electrolytic Reductive Coupling **of 8,s-Diphenylbenzofulvene** with Acrylonitrile.-The catholyte contained 11.5 g. (0.041 mole) of the fulvene, 23.1 g. (0.435 mole) of acrylonitrile, 82.3 **g.** of dimethylformamide, and 27.6 g. of 90.5% aqueous tetraethylammonium p-toluenesulfonate. The anolyte was 20 g. of 60 $\%$ aqueous quaternary salt. Electrolysis was conducted at 40- 45° at a controlled cathode voltage of -1.50 to -1.60 v. (s.c.e.). The amperage was gradually reduced from a high of 1.80 to 0.20 amp., total 2.27 amp.-hr. Acetic acid (1.80 ml.) was used for pH control. At the end of the run the mercury was separated and the brown-red catholyte was run dropwise with stirring into 300 ml. of water. The light yellow precipitate, after air drying overnight, weighed 29.0 g. It was extracted in a Soxhlet with methylene chloride for 11 hr. The insoluble portion was polyacrylonitrile¹⁷; the soluble material (10.8 g.) , an amber sirup, was dissolved in methylene chloride and purified by passage through a column of activated alumina. The effluents were taken to dryness, the residue was digested with methanol, and the suspension was cooled at room temperature and filtered. For analysis a sample was dissolved in acetonitrile and filtered. Addition of methanol precipitated white crystals, m.p. 172- 173".

Anal. Calcd. for C₃₁H₂₇N₃: C, 84.32; H, 6.16; N, 9.52. Found: C, 84.07; H, 6.27; N, 9.57.

(23) C. Weizmann, **E.** Bergmann, and M. Sulzbacker, *J. Ore. Chem.,* **16, 918 (1950).**

The proton magnetic resonance spectrum was determined under the conditions described above except that deuterated chloroform was used as the solvent. The proton of interest in this system is the olefinic proton in the five-membered ring of XIV. This proton appears in the spectrum as a singlet, δ -6.22 . Dressler and Kurland¹⁸ have observed this proton at δ -6.15 in an analogous system. The proton would have appeared as a multiplet had the isomer shown (left) been present.

Electrolytic Reductive Coupling **of** 9-Benzalfluorene **and** Ethyl Acrylate.-The catholyte contained 10.9 g. (0.0429 mole) of benzalfluorene, 42.6 $g(0.426 \text{ mole})$ of ethyl acrylate, 27.8 g . of dimethylformamide, and 61.8 g. of 86.5% aqueous tetraethylammonium p-toluenesulfonate. The anolyte was 20 g. of a 60% aqueous solution of the quaternary salt. Electrolysis proceeded at 40° at a controlled cathode voltage of -1.50 to -1.55 v. $(s.c.e.).$ The amperage was gradually reduced from 1.0 to O.lOamp., tota12.1 amp.-hr. Aceticacid(l.70ml.) wasusedto maintain the pH at *ca. 8.* The catholyte was then diluted with water, the mercury was separated, and 6.5 g. of 9-benzylfluorene, m.p. 133-134", was removed by filtration. The mother liquor was extracted with four 50-ml. portions of methylene chloride. The extracts were washed and dried over Drierite. Volatile materials were removed on the water bath using an aspirator. The residue (5.4 g. of brown solid) yielded 2.2 g. of 9-benzylfluorene on fractional crystallization from methanol. The mother liquor was evaporated, and the residue was dissolved in methylene chloride and purified through alumina. The 2.04 g. of sirup obtained from the eluates was distilled; b.p. 204 $^{\circ}$ (0.4 mm.).

Anal. Calcd. for XV, C₂₅H₂₄O₂: C, 84.23; H, 6.78. Found: C, 83.78; H, 6.79.

The infrared spectrum was consistent with the proposed structure.

Acknowledgment.--All instrumental analyses were performed by Donald Beasecker's group. The proton magnetic spectra were obtained and interpreted by Donald Bauer and Robert Anderson. Infrared spectra were interpreted by Ronald Coffey.

Electrolytic Reductive Coupling. VII.¹ A New Class of Acrylonitrile Oligomers

MANUEL M. BAIZER AND JAMES D. AXDERSON

Central Research Department, Monsanto Company, St. Louis, Missouri 6% 66

Received November 16, 1964

Previous work on the electrolysis of acrylonitrile in aqueous quaternary ammonium salts under mildly alkaline conditions has been extended into the region of high acrylonitrile-water ratios. At very low water concentrations acetone-soluble, relatively low-melting polyacrylonitriles of average mol. wt. 600-1300 an acrylonitrile hydro trimer, 1,3,6-tricyanohexane, and a mixture of hydro tetramers, consisting of 1,3,6,8- and **1,3,5,8-tetracyanooctane.** The structures of these new acrylonitrile oligomers were proved by conversion to and independent synthesis of the corresponding esters. The electrolytic hydropolymerization of acrylonitrile is viewed as proceeding from an initially formed α, α' -adiponitrile dianion.

There is a considerable literature² on the anionic polymerization of acrylonitrile (AN) by *chemical* means *(e.g.,* diethyl sodiomalonate, organolithium compounds, potassium alkoxides, and quaternary ammonium hydroxides³). In all cases, an alien anion, Z, which appears finally as an end group in the polymer, adds to pears imally as an end group in the polymer
AN to produce the initiating carbanion I.
 $Z: + CH_2=CHCN \longrightarrow (ZCH_2CHCN)^-$

$$
Z: + CH_2=CHCN \longrightarrow (ZCH_2CHCN)^-
$$

I

Little has been published on the *electrolytic* carbanionic polymerization of AN.⁴ Sr. M. Murphy and coworkers' observed polymer formation during polarography of AN in anhydrous dimethylformamide. They postulated that the initiating carbanion formed at the cathode is 11, an entity also considered to participate in chain transfer during chemical anionic polymerization.

$$
\begin{array}{c} \mathrm{CH_2} \!\!=\!\!\bar{\mathrm{C}}\text{-}\mathrm{CN} \\ \mathrm{II} \end{array}
$$

⁽¹⁾ Paper **VI: M.** M. Baizer and J. D. Anderson, *J. Org. Chem., 80,* **1348 (1965).**

⁽²⁾ R. R. Cundall, D. D. Eley, and *J.* Worrall, *J. Polymer Sci.,* **68, 869 (1962),** and references cited therein.

⁽³⁾ A. Zilkha, **B.** A. Feit, and M. Frankel, *ibid.,* **4S, 231 (1961).**

⁽⁴⁾ Since the preliminary announcement of our results⁵ related work has been published by Funt and Williams⁶² and by Lazarov, Trifonov, and Vitanov.^{6b}

⁽⁵⁾ M. M. Ba:zer, *Tetrahedron Letters.* **973 (1963).**

⁽⁶⁾ (a) B. L. Funt and F. D. Williams, *J. Polymer Sei., Pt. A,* **2, 865 (1964);** (b) S. Lazarov, **A.** Trifonov, and T. Vi.anov, *Z. Physik. Chem.* (Leipaid, **221 (1964).**

⁽⁷⁾ M. Murphy, M. G. Carangelo, M. B. Ginaine, and M. C. Markham, *J. Polyme? Sci.,* **54, 107 (1961).**