

complexing power than  $K_1$ , because the activity coefficient of Un in water, eq. 2, deviates from unity very much more than it does in carbon tetrachloride, eq. 4.

TABLE IV

COMPARISON OF ARGENTATION CONSTANTS AT 25°			
Hydrocarbon	$K_1$	$K_2$	$K_0 \times 10^3$
3-Hexyne	19.1	0.23	8.2
<i>cis</i> -2-Pentene <sup>19</sup>	112.5		31.2
<i>trans</i> -2-Pentene <sup>19</sup>	62.2		11.1
Cyclohexene <sup>18</sup>	79.3		18.4
Benzene <sup>20</sup>	2.41	0.212	
Naphthalene <sup>1</sup>	2.94	.91	
Phenanthrene <sup>1</sup>	3.55	.99	

3-Hexyne complexes less strongly with silver than do the 2-pentenes<sup>19</sup> and cyclohexene<sup>18</sup> and more strongly than aromatic hydrocarbons<sup>1,20</sup> as shown by the data in Table IV. The fact that alkyl groups depress the argentation reaction in alkenes,<sup>18</sup> in spite of electron release by these groups, may be due in large part to steric factors. Steric effects may well account for the lower constants of *trans*-2-butene<sup>3</sup> and *trans*-2-pentene<sup>19</sup> as compared to their *cis*-isomers.<sup>21</sup> In 3-hexyne the steric effect presumably would be more than in a corresponding *cis*-alkene,<sup>4</sup> and probably comparable to that in the *trans* isomer.

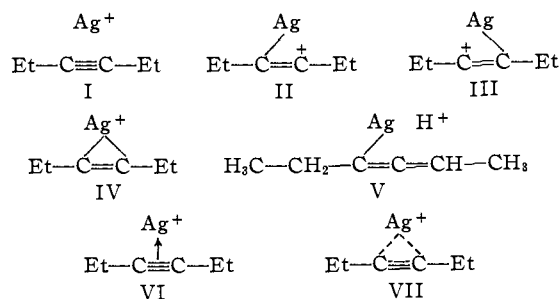
**Nature of the Complex.**—The 3-hexyne-silver ion complex, like the silver-olefin and mercury-hexyne<sup>23</sup> complexes, is a resonance hybrid. The

(20) L. J. Andrews and R. M. Keefer, *THIS JOURNAL*, **71**, 3644 (1949).

(21) M. J. S. Dewar, *Bull. soc. chim.*, C71 (1951), believes that an alkyl group lessens the stability of a complex through its effect on the anti-bonding  $\pi$ -molecular orbitals of an olefin in the formation of the second bond between a heavy metal and an olefin.

(22) According to N. Koenig, Ph.D. Thesis, California Institute of Technology, 1950, this would be silver(I)-3-hexynium ion. The salt in solution would be silver(I)-3-hexynium nitrate.

(23) H. Lemaire and H. J. Lucas, *THIS JOURNAL*, **77**, 939 (1955).



main contributing forms are I, II, III and IV; other forms, presumably less important, arise from hyperconjugation, V.<sup>24</sup> Other ways of representing the complex are based on the formulations of Dewar, VI,<sup>25</sup> and Winstein, VII.<sup>26</sup> The structure of the 3-hexyne-silver ion complex is similar to that of the 3-hexyne-acetoxymercurinium ion,<sup>23</sup> the intermediate in the mercury-catalyzed reaction of 3-hexyne with acetic acid.

The 3-hexyne-silver complex is less stable than the complex of cyclohexene, but probably is more stable than that of a *trans*-hexene, for which an approximate value of 5 to  $7 \times 10^{-3}$  is reached by considering the respective values of *cis*- and *trans*-2-pentene, Table IV, those of *cis*- and *trans*-2-butene<sup>3</sup> ( $73.0 \times 10^{-3}$  and  $25.2 \times 10^{-3}$ , respectively), the trend in these values, and the *cis/trans* ratios of 2.8 and 2.9 for the pentenes and butenes, respectively. This rough estimate, 5 to  $7 \times 10^{-3}$ , is substantiated by a second estimate from cyclohexene,  $K_0 = 18.4 \times 10^{-3}$ , by assuming a *cis/trans* ratio of 2.7 for the hexenes. This gives a value of  $6.8 \times 10^{-3}$  for the  $K_0$  of a *trans*-hexene.

(24) Proposed by A. E. Comyns.

(25) M. J. S. Dewar, *J. Chem. Soc.*, 406 (1946); see also A. D. Walsh, *Nature*, **169**, 165, 712 (1947).

(26) S. Winstein and co-workers, *THIS JOURNAL*, **74**, 1133, 1160 (1952).

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[CONTRIBUTION FROM THE RESEARCH CENTER, THE B. F. GOODRICH CO.]

## Vinylidene Cyanide. VII. Copolymerization<sup>1a</sup>

BY HARRY GILBERT,<sup>1b</sup> F. F. MILLER, S. J. AVERILL, E. J. CARLSON, V. L. FOLT, H. J. HELLER, F. D. STEWART, R. F. SCHMIDT AND H. L. TRUMBULL

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Vinylidene cyanide copolymerizes readily with a wide range of common monomers. The Mayo-Lewis copolymerization equation is solved for 15 systems. The relative reactivities of the comonomers toward the vinylidene cyanide free radical are listed. The most active comonomers are styrene, chlorobutadiene, dichlorostyrene, and methyl methacrylate. The least active comonomers are acrylic acid, vinyl chloride, dichloroethylene and maleic anhydride. Vinyl ether-vinylidene cyanide systems give a novel autocatalytic ionic polymerization. The styrene-vinylidene cyanide system exhibits a rapid free radical cross-initiation. The Price-Alfrey  $Q$  and  $e$  parameters for vinylidene cyanide are calculated. The near-quantitative nature of the  $Q-e$  concept is rather strongly confirmed by the data.

The homopolymerization of vinylidene cyanide (I) has been reported previously.<sup>2</sup> The present

(1) (a) This paper was presented before the Division of Polymer Chemistry at 126th Meeting of the American Chemical Society in New York, N. Y., September 14, 1954. (b) B. F. Goodrich Chemical Co., Avon Lake, Ohio.

(2) H. Gilbert, F. F. Miller, S. J. Averill, R. F. Schmidt, F. D. Stewart and H. L. Trumbull, Part III, *THIS JOURNAL*, **76**, 1074 (1954).

paper describes the copolymerization of I with sixteen vinyl monomers and one diene. Another objective of this work was to check the quantitative nature of the Price-Alfrey<sup>3</sup> " $Q$ " and " $e$ " method for correlating resonance stabilization and polarity with relative reactivities of monomers toward free radicals.

(3) C. C. Price, *J. Polymer Sci.*, **3**, 772 (1948).

TABLE I  
 FREE RADICAL MONOMER REACTIVITY RATIOS WITH VINYLIDENE CYANIDE

System	Comonomer ( $M_2$ )	$r_1^a$	$r_2$	$r_1 r_2$	$1/r_1$
1	Styrene	0.001 (0.007-0.004 <sup>b</sup> )	0.005 (0.003-0.009 <sup>b</sup> )	$5.0 \times 10^{-6}$	1000
2	2-Chlorobutadiene-1,3	.0048 (0.0032-0.010)	.016 (0.0097-0.048)	$7.7 \times 10^{-5}$	208
3	2,5-Dichlorostyrene	.0092 (0.0057-0.010)	.031 (0.024-0.042)	$2.8 \times 10^{-4}$	110
4	Methyl methacrylate	.031 (0.023-0.077)	.046 (0.035-0.11)	$1.4 \times 10^{-3}$	32
5	Vinylidene chloride	.049 (0.043-0.17)	.012 (0.007-0.25)	$5.9 \times 10^{-4}$	20
6	Methyl $\alpha$ -chloroacrylate	.091 (0.064-0.14)	.41 (0.27-0.55)	$3.7 \times 10^{-2}$	11
7	Vinyl benzoate	.10 (0.081-0.51)	.008 (0.008-0.07)	$8.0 \times 10^{-4}$	10
8	Vinyl acetate	.11 (0.073-0.20)	.0054 (0.0026-0.013)	$5.9 \times 10^{-4}$	9.1
9	Vinyl chloroacetate	.13 (0.08-0.18)	.00 (0.00-0.004)	.....	7.7
10	2-Chloropropene	.20 (0.14-0.26)	.00 (0.00-0.00)	.....	5.0
11	Acrylic acid	.29 (0.21-0.37)	.26 (0.20-0.32)	$7.5 \times 10^{-2}$	3.5
12	Vinyl chloride	.54 (0.23-0.72)	.017 (0.007-0.040)	$9.2 \times 10^{-3}$	1.9
13	<i>cis</i> -Dichloroethylene	30 (20-50)	.0	.....	0.03
14	<i>trans</i> -Dichloroethylene	30 (20-50)	.0	.....	.03
15	Maleic anhydride	45 (35-65)	.0	.....	.02

<sup>a</sup> The subscript 1 refers to vinylidene cyanide. <sup>b</sup> These values were determined as indicated in Fig. 5. They are not probable errors, but rather maximum deviations. An objective and quantitative method for calculating the probable errors of  $r$ -values is simply not available. The differential form of the copolymer equation was solved by the curve fitting method, by the method of least squares or by a graphical procedure as indicated in the Experimental section (see tabulation of polymerization data).

### Results and Discussion

In Table I and Figs. 1 to 5 are shown the solutions to the copolymerization equation<sup>4</sup> for fifteen copolymer systems. The monomer reactivity ratios ( $r_1$  and  $r_2$ ), the  $r_1 r_2$  products, and the relative reactivities ( $1/r_1$ ) of these monomers toward the vinylidene cyanide chain radical are listed. All of the  $r$ -values were not determined at the same temperature (see data for systems 1-15), but no effect of temperature upon  $r$ -values was found in the range studied (0-50°). Note especially in system 1 where the data for two tubes run at 0° fit the curve very well although the other tubes in this system were run at 45°. The most active comonomers (styrene,

2-chlorobutadiene-1,3, 2,5-dichlorostyrene and methyl methacrylate) all have electron-rich<sup>5</sup> double bonds. The least active comonomers (acrylic acid, vinyl chloride, dichloroethylene and maleic anhydride) all have electron-poor double bonds.

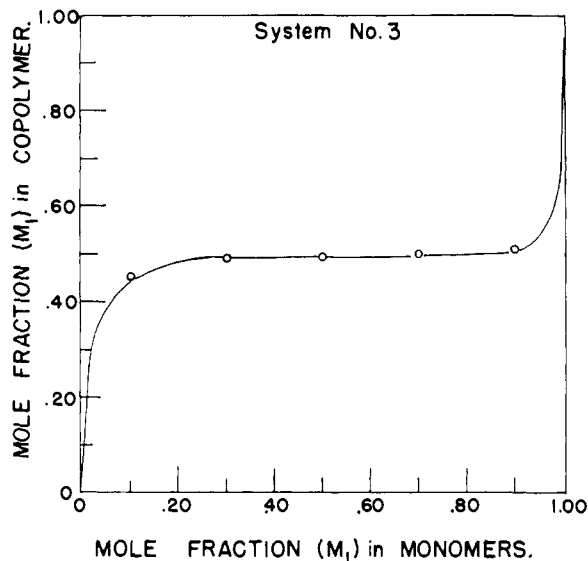


Fig. 1.—Copolymer composition curve for system 3. The curve represents the solution to the copolymer equation when  $r_1 = 0.0092$ ,  $r_2 = 0.031$ . The open circles are the experimental points, ( $M_1$ ) is vinylidene cyanide and the comonomer is 2,5-dichlorostyrene.

(4) F. R. Mayo and F. M. Lewis, THIS JOURNAL, 66, 1594 (1944).

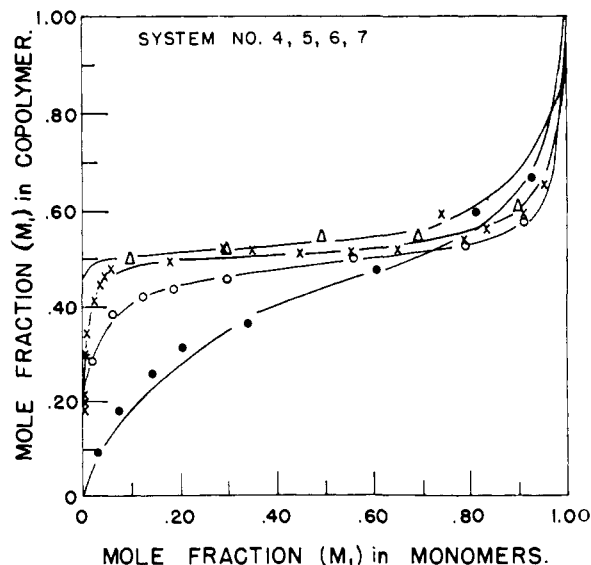


Fig. 2.—Copolymer composition curves for systems 4, 5, 6 and 7: O, system 4,  $r_1 = 0.031$ ,  $r_2 = 0.046$ ; X, system 5,  $r_1 = 0.049$ ,  $r_2 = 0.012$ ; ●, system 6,  $r_1 = 0.091 \pm 0.050$ ,  $r_2 = 0.41 \pm 0.14$ ; Δ, system 7,  $r_1 = 0.10$ ,  $r_2 = 0.008$ . See Table I for identification of comonomers.

The data for the dichloroethylenes and for maleic anhydride show a very poor fit to the copolymerization equation. The mother liquors from these systems were examined carefully for soluble polymers but none was found.

No " $r$ "-values are given for the vinylidene cyanide:vinyl ether systems since the data (systems 16

(5) C. C. Price, "Mechanisms of Reactions at Carbon-Carbon Double Bonds," Interscience Publishers, Inc., New York, N. Y., 1946 p. 96.

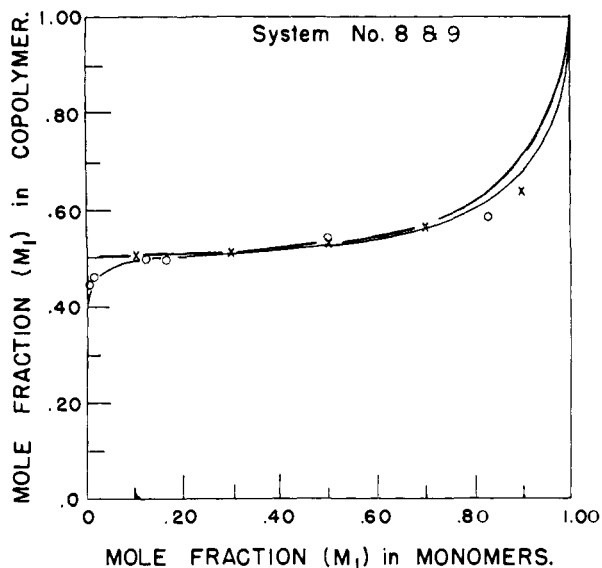


Fig. 3.—Copolymer composition curves for systems 8 and 9: O, system 8,  $r_1 = 0.11$  ( $0.20 \geq r_1 \geq 0.073$ ),  $r_2 = 0.0054$  ( $0.0135 \geq r_2 \geq 0.0026$ ); X, system 9,  $r_1 = 0.13 \pm 0.05$ ,  $r_2 = 0.00$  ( $r_2 \leq 0.004$ ).

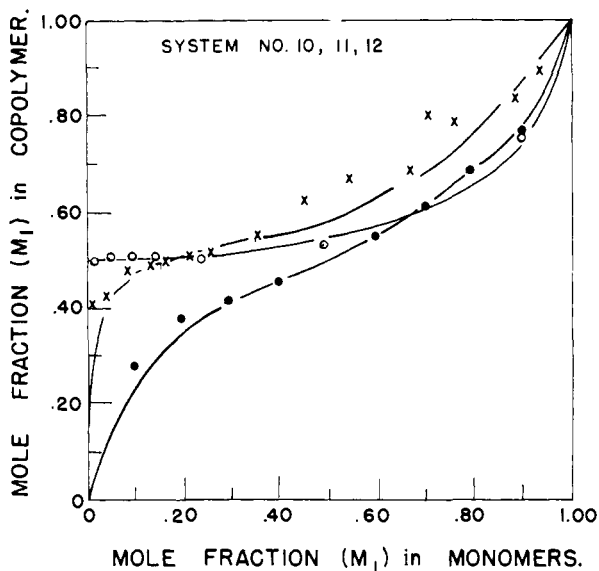


Fig. 4.—Copolymer composition curves for systems 10, 11 and 12: O, system 10,  $r_1 = 0.20 \pm 0.06$ ,  $r_2 = 0.00$ ; ●, system 11,  $r_1 = 0.29 \pm 0.08$ ,  $r_2 = 0.26 \pm 0.06$ ; X system 12,  $r_1 = 0.54$  ( $0.23 \leq r_1 \leq 0.72$ ),  $r_2 = 0.017$  ( $0.040 \geq r_2 \geq 0.0071$ ).

and 17) do not permit solving the copolymerization equation. Rapid ionic polymerization apparently precludes the possibility of free-radical initiation. The vinyl ethers are as sensitive to cationic initiation<sup>6a,b</sup> as the vinylidene cyanide is toward anionic initiation.<sup>2</sup> Evidently the ether acts as a base toward I while I acts as an acid toward the ether. The net result is a novel situation wherein the mixture of the two monomers results in simultaneous

(6) (a) E. R. Blout and H. Mark, "Monomers," Interscience Publishers, Inc., New York, N. Y., 1951, pp. 16, 37 of Chapter on Vinyl Ethers; (b) D. D. Eley and A. W. Richards, *Trans. Faraday Soc.*, **45**, 425 (1949).

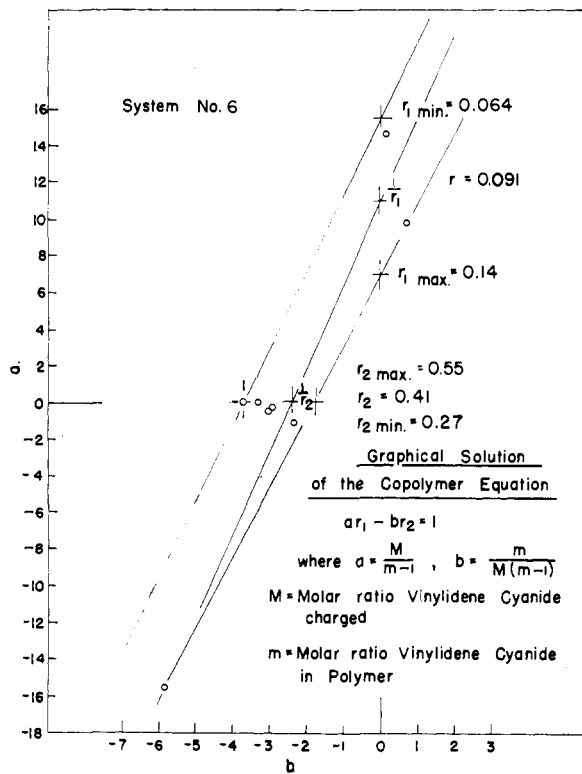


Fig. 5.—Example of the graphical solution of the copolymer equation using the data of system 6.

cationic and anionic polymerizations. Two polymers were always isolated from these mixtures: a benzene-soluble polymer high in vinyl ether content, and a benzene-insoluble polymer high in vinylidene cyanide content. The formation of the soluble polymer can be inhibited completely by the addition of triethanolamine to the vinyl ether prior to the addition of I. The formation of the insoluble polymer can be stopped by the addition of phosphorus pentoxide to I prior to the addition of the vinyl ether. Triethanolamine is a known inhibitor for the cationic polymerization of vinyl ethers, while phosphorus pentoxide is a known inhibitor for the anionic polymerization of I.

The strong tendency of vinylidene cyanide to alternate during copolymerization is immediately apparent from the data in Table I. Six of the copolymer systems have  $r_1 r_2$  products of less than  $9.0 \times 10^{-4}$ . The only poor alternating systems are the dichloroethylenes with I and maleic anhydride with I. Any monomers having polarities similar to I would, of course, not be expected to alternate with I.

Of the monomers studied, styrene has the greatest reactivity toward the vinylidene cyanide free radical. The styrene monomer is 50,000 times more reactive than maleic anhydride. The *cis*- and *trans*-dichloroethylenes have about the same minimum reactivity as maleic anhydride. The 2,5-dichlorostyrene shows about one-tenth the reactivity of styrene. Methyl  $\alpha$ -chloroacrylate, vinyl benzoate and vinyl acetate add to the vinylidene cyanide free-radical at about equal rates (one-hundredth of the styrene rate). Vinylidene chlo-

POLYMERIZATION DATA					System 7: Vinylidene cyanide with vinyl benzoate <sup>a,q</sup> at 43°				
[M] <sup>b</sup>	Time, hr.	Conversion, %	Nitrogen, %	[ $\eta$ ] <sup>c</sup>	0.10	17	13	11.87	0.484 <sup>ii</sup>
System 1: Vinylidene cyanide with styrene <sup>a,f</sup> at 45°					.30	17	17	12.65	.509
0.10	0.33	2.33	15.13	0.493	.50	17	17	13.41	.531
.15	0.20	4.00	15.21	.496	.70	17	15	13.70	.542
.167	23.0 <sup>d</sup>	11.0	15.82	.512	.90	17	5.6	15.62	.595
.500	23.0 <sup>d</sup>	29	16.00	.516 <sup>e</sup>	System 8: Vinylidene cyanide with vinyl acetate <sup>u,r</sup> at 45°				
.576	24.0 <sup>d</sup>	5.0	15.40	.501	0.010	2.25	0.30	14.91	0.439
.700	0.30	8.36	15.39	.500	.020	.75	2.68	16.05	.470
.80	.33	5.61	15.41	.501	.124	.50	2.58	16.85	.494
.90	.50	2.64	15.51	.504	.170	.66	3.08	16.87	.494
System 2: Vinylidene cyanide with 2-chlorobutadiene-1,3 <sup>g,f</sup> at 40°					.500	.83	8.58	18.40	.540
0.091	3.0	15	16.02 <sup>h</sup>	0.477	.830	1.66	4.64	19.97	.580
.305	3.0	18	16.09 <sup>h</sup>	.481	System 8: Using anionic initiators <sup>v</sup> at 20°				
.500	16.5	46	16.46 <sup>h</sup>	.489	0.170 <sup>w</sup>	18	10	31.4	0.900
.708	16.5	28	16.86 <sup>h</sup>	.501	.500 <sup>w</sup>	18	15	33.3	.940
System 3: Vinylidene cyanide with 2,5-dichlorostyrene <sup>i,f</sup> at 40°					.710 <sup>z</sup>	0.01	20	33.7	.947
0.100	3.5	1.8	9.31	0.453 <sup>j</sup>	.830 <sup>w</sup>	24	10	34.5	.970
.100	2.0	4.8	9.86		System 9: Vinylidene cyanide with vinyl chloroacetate <sup>u,r</sup> at 40°				
.300	2.0	2.1	10.62	0.485	0.10	0.516	5.62	14.14	0.501
.500	2.0	4.7	10.88	.492 <sup>j</sup>	.30	.516	5.69	14.58	.514
.700	2.0	4.4	10.63	.501 <sup>j</sup>	.50	.90	9.56	15.32	.535
.900	8.2	14	10.95		.70	1.33	4.73	16.40	.565
.900 <sup>d</sup>	8.2	10	10.77	0.519	.90	4.50	3.80	19.09	.637
.900 <sup>t</sup>	2.0	10.6	11.40		System 10: Vinylidene cyanide with 2-chloropropene <sup>m,r,t</sup> at 40°				
System 4: Vinylidene cyanide with methyl methacrylate <sup>m,f</sup> at 50°					0.0196	2.75	0.24	17.78	0.490
0.025	21	3.70	8.22	0.275	.0491	1.75	0.83	18.20	.501
.063	21	4.65	11.85	.381	.0983	1.75	1.18	18.39	.506
.124	2.66	4.20	13.09	.424	.148	1.75	1.00	18.43	.507
.184	2.83	4.40	13.39	.432	.246	1.75	2.05	17.96	.494
.300	3.0	5.45	14.21	.456	.495	1.75	0.60	19.50	.532
.562	21.0	8.10	15.79	.501	.898	4.40	3.6	27.74	.768
.794	25.0	7.10	16.53	.522	System 11: Vinylidene cyanide with acrylic acid <sup>m,r,t</sup> at 50°				
.921	33.0	5.60	18.54	.578	0.10	7.25	0.6	10.54	0.277
System 5: Vinylidene cyanide with vinylidene chloride <sup>m,g,t</sup> at 22°					.20	7.25	0.8	14.12	.374
0.00617	16	0.83	6.73	0.222 <sup>ii</sup>	.30	32	2.8	15.84	.421
.00821	16	.52	9.06	.295 <sup>ii</sup>	.40	32	1.7	17.12	.457
.0124	16	.66	10.53	.340	.60	32	4.6	20.70	.557
.0247	16	1.16	12.85	.409	.70	32	2.0	22.69	.613
.0614	16	1.32	15.17	.476	.80	32	0.3	25.29	.687
.179	20.5	0.38	15.86	.495	.90	32	1.9	28.20	.772
.347	16	9.45	16.35	.509	1.00	32	0.4	32.70 <sup>z</sup>	.910
.554	16	19.25	16.53	.514	System 12: Vinylidene cyanide with vinyl chloride <sup>m,r,t</sup> at 50°				
.743 <sup>p</sup>	25.5 <sup>n</sup>	1.7	19.27	.590	0.0404	8.0	3.35	17.79	0.440 <sup>ii</sup>
.832 <sup>p</sup>	36.75 <sup>n</sup>	1.5	18.03	.556	.0817	8.0	4.00	19.36	.483 <sup>ii</sup>
.917 <sup>p</sup>	38.25 <sup>n</sup>	3.0	19.48	.595	.123	8.0	4.35	19.71	.493
System 6: Vinylidene cyanide with methyl $\alpha$ -chloroacrylate <sup>m,r</sup> at 50°					.166	8.0	5.59	20.01	.502
0.030	0.75	5.16	2.05	0.0856	.210	8.0	7.0	20.25	.508
.030	0.75	4.04	2.27	.0943	.255	8.0	7.75	20.75	.523
.075	1.25	8.40	4.31	.174	.348	8.0	15.75	22.02	.559
.146	1.25	7.20	6.33	.248	.444	1.0	3.1	24.09	.620
.214	1.25	9.30	8.02	.307	.545	1.25	4.50	25.95	.676
.340	1.25	9.45	9.45	.355	.667	1.00	3.50	26.44	.691
.606	1.50	7.30	13.21	.473	.706	0.50	7.20	30.39	.815
.816	2.50	4.90	17.40	.592	.878	0.50	6.40	31.33	.846
.932	6.77	10	19.72	.659					

POLYMERIZATION DATA (Continued)				
[M] <sup>b</sup>	Time, hr.	Conversion, %	Nitrogen, %	[m] <sup>c</sup>
System 13: Vinylidene cyanide with <i>cis</i> -dichloroethylene <sup>m,f</sup> at 40°				
0.0614	24.75	0.08	25.33	0.749
.121	21.0	0.98	32.63	.926
.121	21.0	1.10	32.23	.915
.293	21.0	0.25	31.86	.907
.554	21.0	6.2	33.62	.947
.786	21.0	5.7	33.77	.952
.919	21.0	8.2	33.46	.944
System 14: Vinylidene cyanide with <i>trans</i> -dichloroethyl- ene <sup>m,f</sup> at 40°				
0.0614	295	0.05	27.85	0.811
.121	311	.58	30.29	.870
.180	295	.15	31.32	.895
.293	295	2.25	32.55	.924
.554	71	0.40	32.71	.927
.786	71	4.5	33.62	.948
.919	72	2.4	32.77	.928
System 15: Vinylidene cyanide with maleic anhydride <sup>a,g</sup> at 50°				
0.123	116	1.0	31.05	0.890
.239	116	0.20	31.61	.903
.350	116	8.2	32.15	.916
.456	116	12.3	32.24	.918
.557	116	13.7	32.33	.920
.653	116	15.6	32.82	.932
.746	116	16.0	33.17	.938
.834	72	0.80	33.37	.942
.919	72	1.2	33.84	.954
System 16: Vinylidene cyanide with vinyl isobutyl ether <sup>b,b</sup> at 0°				
0.17 <sup>cc</sup>	0.25	69 <sup>dd</sup>	0.88	0.030
		4.3 <sup>dd</sup>	23.0	.695
System 17: Vinylidene cyanide with vinyl butoxyethyl ether at 25°				
0.300 <sup>pp</sup>	18	70.7 <sup>ee</sup>	2.47	0.121
		16.8 <sup>ff</sup>	25.37	.817
.379 <sup>pp</sup>	18	70.2 <sup>ee</sup>	2.95	.142
		23.3 <sup>ff</sup>	26.36	.836
.461 <sup>pp</sup>	18	53.4 <sup>ee</sup>	3.52	.167
		28.8 <sup>ff</sup>	27.69	.861
.588 <sup>pp</sup>	18	53.1 <sup>ee</sup>	6.87	.304
		36.6 <sup>ff</sup>	28.45	.877
.681 <sup>hh</sup>	18	...	...	...

<sup>a</sup> All tubes in this system contain 66 vol. % benzene and 0.5% 2,4-dichlorobenzoyl peroxide based on total monomers unless noted otherwise. <sup>b</sup> Mole fraction vinylidene cyanide charged. <sup>c</sup> Mole fraction vinylidene cyanide in polymer calculated from nitrogen analysis unless otherwise noted. <sup>d</sup> Initiator purposely omitted from these tubes. The [M] 0.167 and 0.500 tubes were kept at 0° instead of 45°. <sup>e</sup> A duplicate tube prepared with 1.0% hydroquinone gave nearly identical results in conversion and polymer analysis. This copolymerization can be stopped by high (5 to 10%) concentrations of *t*-butyl hydroquinone. <sup>f</sup> *r*-Values for this system were determined by the curve fitting method of Turner Alfrey, Jr., as described in "Copolymerization" by T. Alfrey, J. J. Bohrer and H. Mark, Interscience Publishers, Inc., New York N. Y., 1952, p. 16. <sup>g</sup> All tubes in this system contain 90% benzene and 0.5% *o,o'*-dichlorobenzoyl peroxide based on total monomers. <sup>h</sup> Chlorine determinations were also run on all four of these polymers: at [M] 0.091, found 21.94% Cl which gives [m] of 0.490; at [M] 0.305, found 21.97% Cl which gives [m] of 0.490; at [M] 0.500, found 21.53% Cl which gives

[m] of 0.495; at [M] 0.708, found 21.05% Cl which gives [m] of 0.507. Average values of [m] from nitrogen and chlorine were used in the determination of *r*-values. <sup>i</sup> All tubes in this system contain 75% benzene and 0.10% *o,o'*-dichlorobenzoyl peroxide based on total monomers. <sup>j</sup> These [m] values are the average values calculated from both the % Cl and % N in the polymers: at [M] 0.100, 4.8% conv., found 29.05% Cl which gives [m] of 0.476; at [M] 0.500, 4.7% conv., found 28.32% Cl which gives [m] of 0.494; at [M] 0.700, 4.4% conv., found 27.68% Cl which gives [m] of 0.517; at [M] 0.900, 14.0% conv., found 26.77% Cl which gives [m] of 0.542; at [M] 0.900, 10.0% conv., found 26.82% Cl which gives [m] of 0.543; at [M] 0.900, 10.6% conv., found 26.98% Cl which gives [m] of 0.536. <sup>k</sup> Initiator and diluent purposely omitted from this tube. <sup>l</sup> All tubes in this system contain 0.15% *o,o'*-dichlorobenzoyl peroxide. No diluent was used in any of these tubes. <sup>m</sup> These tubes were held at 25° for the first 18.5 hr., then at 50° for the balance of the time. <sup>n</sup> Used 20 ml. of benzene per 10 g. of total monomers in these tubes. <sup>o</sup> *r*-Values for this system were determined by the method of least squares. <sup>p</sup> These *r*-values were determined graphically by first putting the copolymer equation in the form:  $(M/(m-1))r_1 - (m/M(m-1))r_2 = 1$ ; let  $(M/m-1) = a$ ,  $m/(M(m-1)) = b$ , then plot *a* vs. *b* and draw the best straight line through the points. *M* is molar ratio of vinylidene cyanide charged and *m* is molar ratio of vinylidene cyanide in the polymer. The limits on the *r*-values were determined by drawing lines of minimum and maximum slope through the plotted points (see Fig. 5). These limits do not represent probable errors, but rather maximum deviations. This procedure is similar to the method of M. Fineman and S. D. Ross, *J. Polymer Sci.*, 5, 269 (1950). <sup>q</sup> All tubes in this system contain 0.10% *o,o'*-dichlorobenzoyl peroxide on total monomers and 75% benzene diluent. <sup>r</sup> Data were obtained from additional polymerizations and have been used in determining the *r*-values, but are not included in the table. <sup>s</sup> All tubes in this system contain 0.2% *o,o'*-dichlorobenzoyl peroxide on total monomers and 20% benzene as diluent unless otherwise noted. <sup>t</sup> The sensitivity of vinylidene cyanide to anionic initiation is shown in these four tubes. <sup>u</sup> No added catalyst in these tubes. The anionic initiation is due to impurities in the vinyl acetate used. <sup>v</sup> The initiator is 0.1% *p*-methoxyphenyldiazothionaphthalene. <sup>w</sup> All tubes in this system contain 0.50% *o,o'*-dichlorobenzoyl peroxide. No diluent was used. <sup>x</sup> The theoretical nitrogen content of polyvinylidene cyanide is 35.89%. This low value of 32.70 is typical for polymers that have been exposed to atmospheric moisture. See reference 1 for a discussion of the degradation of polyvinylidene cyanide. <sup>y</sup> All tubes in this system contain 0.33% caproyl peroxide and 70% benzene diluent. <sup>z</sup> WARNING: a mixture of vinylidene cyanide and vinyl isobutyl ether in the absence of diluents polymerizes with explosive violence. <sup>aa</sup> This polymerization was run in an open tube immersed in an ice-water bath. The ether was dissolved in 25 ml. of benzene. The vinylidene cyanide was then added cautiously. Within 15 minutes the temperature had risen to 30°. <sup>ab</sup> Two polymers were isolated from this system. The 69% conversion represents the benzene soluble polymer. The 4.3% conversion is a benzene-insoluble polymer. <sup>ac</sup> Conversion to polymer soluble in benzene. These polymers were all thick liquids. Their inherent viscosities measured in ethanol at 25° at *c* = 0.4 g./100 ml. were 0.047, 0.047, 0.032 and 0.064 for the four tubes, respectively. <sup>ad</sup> Conversion to polymer insoluble in benzene. These polymers were all tan powders. Their inherent viscosities measured in propylene carbonate at 24.4° at *c* = 0.4 g./100 ml. were 0.94, 0.96, 1.0 and 0.96 for the four tubes, respectively. <sup>ae</sup> No initiator was added to any of these tubes. The diluent was benzene, 82.6, 84.7, 87.8 and 90.9 vol. %, respectively, in the four tubes. The order of addition to the individual tubes was benzene, the vinyl ether, then the vinylidene cyanide. <sup>af</sup> No diluent was used in this tube. The result was a violent polymerization. The reaction started about one second after the two monomers were mixed at room temperature. It was complete in about 5 seconds. The polymer was partially decomposed by the heat of reaction, so no further data were obtained on this charge. <sup>ag</sup> These tubes were inadvertently left in the constant temperature bath too long in that the concentration of monomeric vinylidene cyanide had changed considerably due to the high vinylidene cyanide content of the polymer formed. The

data from these tubes probably should not have been used for determining  $r$ -values without correction for the high conversions.

ride is ten times more reactive than vinyl chloride toward I, which is in the same order as their reported<sup>7</sup> reactivity toward the acrylonitrile radical.

The vinylidene cyanide:styrene and the vinylidene cyanide:dichlorostyrene systems exhibit a rapid "cross" initiation of the type predicted by Walling.<sup>8</sup> His measurements of the rates of the uncatalyzed copolymerization of styrene:methyl methacrylate indicated a bimolecular initiation which was more rapid than the bimolecular initiation of either monomer alone. Walling predicted that much larger values of the specific rate of cross-initiation might be expected for more strongly alternating pairs of monomers. The system vinylidene cyanide:styrene is very strongly alternating; and the free radical copolymerization does proceed readily at room temperature in the absence of catalysts. In fact, it can only be stopped by high concentrations of oil-soluble inhibitors such as *t*-butyl hydroquinone.<sup>9</sup>

TABLE II  
VINYLIDENE CYANIDE "e" AND LOG "Q" VALUES

Comonomer (M <sub>2</sub> )	e <sub>2</sub>	log Q <sub>2</sub>	Vinylidene cyanide (M <sub>1</sub> )	
			e <sub>1</sub>	log Q <sub>1</sub>
Styrene	-0.8	0.00 <sup>a</sup>	2.7	1.1
Vinyl chloride	.3	-1.30 <sup>a</sup>	2.5	0.82
Vinyl acetate	-.3	-1.52 <sup>a</sup>	2.4	0.34
Vinylidene chloride	.6	-0.70 <sup>a</sup>	3.3	1.87
Methyl methacrylate	.4	-0.13 <sup>a</sup>	2.9	1.51
Acrylic acid	.8	-0.05 <sup>b</sup>	2.4	1.08
Methyl $\alpha$ -chloroacrylate	.7	-0.46 <sup>c</sup>	2.5	0.47
Vinyl benzoate	.0	-1.6 <sup>d</sup>	2.7	0.50
2,5-Dichlorostyrene	.4	0.22 <sup>a</sup>	2.5	0.46
Average values from the nine copolymer systems:			e <sub>1</sub> = 2.7	log Q <sub>1</sub> = 0.91

<sup>a</sup> "e" and "Q" values from C. C. Price's monomer map, *J. Polymer Sci.*, **3**, 772 (1948). <sup>b</sup> Acrylic acid "e" and "Q" values calculated from the system: acrylic acid ( $r$  0.25), styrene<sup>10</sup> ( $r$  0.15,  $e$  -0.8,  $\log Q$  0.0). <sup>c</sup> Average values calculated from three systems: methyl  $\alpha$ -chloroacrylate ( $r$  0.25), styrene<sup>11</sup> ( $r$  0.30); methyl  $\alpha$ -chloroacrylate ( $r$  0.3), methyl methacrylate<sup>12</sup> ( $r$  1.2); methyl  $\alpha$ -chloroacrylate ( $r$  0.15), acrylonitrile<sup>12</sup> ( $r$  0.20,  $e$  1.1,  $\log Q$  -0.3). <sup>d</sup> Average values calculated from the systems: vinyl benzoate ( $r$  0.05), acrylonitrile<sup>10</sup> ( $r$  5.0); vinyl benzoate ( $r$  0.1), vinylidene chloride<sup>10</sup> ( $r$  7.0).

In Table II are listed the results of nine independent calculations of the Price-Alfrey "e"- and "Q"-values for vinylidene cyanide. These nine copolymer systems were chosen because they were considered as having the most accurate "r"-values of the fifteen systems studied.

(7) F. R. Mayo, F. M. Lewis and C. Walling, *THIS JOURNAL*, **70**, 1529 (1948).

(8) Cheves Walling, *ibid.*, **71**, 1930 (1949).

(9) In the presence of 10% *t*-butylhydroquinone, the vinylidene cyanide:styrene system produces a crystalline trimer. It melts sharply at 160-161° and analyzes 21.49% N. J. B. Hoertz found that alkaline potassium permanganate oxidation of the trimer yields phthalic acid. It is most probably 1-(2,2-dicyanoethyl)-4,4-dicyano-1,2,3,4-tetrahydronaphthalene.

(10) E. C. Chapin, *et al.*, *J. Polymer Sci.*, **4**, 497 (1949).

(11) R. C. Fordyce and E. C. Chapin, *THIS JOURNAL*, **69**, 581 (1947).

(12) T. Alfrey, *et al.*, *J. Polymer Sci.*, **5**, 719 (1950).

The "Q", "e" defining equations

$$r_1 = \frac{Q_1}{Q_2} \exp[-e_1(e_1 - e_2)] \quad (1)$$

$$r_2 = \frac{Q_2}{Q_1} \exp[-e_2(e_2 - e_1)] \quad (2)$$

were transposed into the following form to simplify their solution

$$2.303 \log r_1 r_2 = -(e_1 - e_2)^2 \quad (1a)$$

$$\log Q_1 = \log r_1 + \log Q_2 + \frac{e_1(e_1 - e_2)}{2.303} \quad (2a)$$

The known  $r_1 r_2$  product (see Table I) and the  $e_2$ -value of the comonomer (see Table II) were inserted in equation 1a which was then solved for  $e_1$ . Equation 2a was then solved for  $\log Q_1$ .

The average "e<sub>1</sub>"-value is 2.7 (max. 3.3, min. 2.4). The average  $\log$  "Q<sub>1</sub>" value is 0.91 (max. 1.87, min. 0.34). The highest "e"-value monomer previously reported is fumaronitrile<sup>13</sup> with a value of 2.1.<sup>14</sup> The vinylidene cyanide "e<sub>1</sub>"-values in Table II are remarkably constant, while the "Q<sub>1</sub>"-values show a rather large spread.<sup>15</sup>

The high "e"- and "Q"-values of vinylidene cyanide are consistent with the structure of the monomer, since the two nitrile groups on the one carbon atom cause considerable polarization<sup>5</sup> of the  $\pi$ -electrons of the double bond of the olefin while at the same time providing sites for an odd electron on the vinylidene cyanide radical.

All of the copolymerizations for which monomer reactivity ratios are herein reported were initiated by free-radical initiators. Because of the ease with which vinylidene cyanide undergoes anionic initiation, the selection of initiators, the solvent medium and the purification of the comonomers are much more critical than in ordinary polymerizations. Chlorinated benzoyl peroxides were selected as the best initiators. They contain no potentially basic atoms and dissociate into free radicals readily at 30 to 50° in solution. An initiator such as *p*-methoxyphenyldiazothionaphthalene is entirely unsuitable (see data under system 8). Benzene was selected as the best solvent medium because of its low dielectric constant. The purity of the comonomers was checked by running control tubes without initiator, placed in the constant temperature bath along with the catalyzed tubes. If these were free of polymer at the time the catalyzed tubes were pulled from the bath, anionic initiation was considered absent. This procedure was useless in the styrene and the dichlorostyrene systems 1 and 3, respectively, because of the free-radical cross-initiation. The fastest polymerizations occurred with monomers having polarities opposite to vinylidene cyanide. These fast monomers were styrene, vinyl

(13) M. C. de Wilde and G. Smets (*ibid.*, **5**, 253 (1950)) report an "e"-value for maleic anhydride of -2.65 which is probably a misprint. Our calculations of the "e"-value using their data gives +2.67 average "e" from the three systems they studied.

(14) C. C. Price and R. D. Gilbert, *J. Polymer Sci.*, **8**, 577 (1952).

(15) It can be shown mathematically that the relative errors in the "r"-values are magnified much more in the  $\log$  "Q"-values than in the "e"-values. Assuming that the relative errors in  $r_1$  and  $r_2$  are inversely proportional to their absolute values, then in the system vinylidene cyanide:vinyl acetate the relative error in the  $\log$  "Q<sub>1</sub>" is fourteen times greater than the relative error in "e<sub>1</sub>." An additional reason for the non-constancy of the "Q" values may be the fact that the polymerizations were non-homogeneous.

benzoate and vinyl acetate. The monomers whose polarities are similar to vinylidene cyanide polymerized the slowest. In fact, they were as sluggish as a free radical homopolymerization of vinylidene cyanide. These slow monomers were maleic anhydride, dichloroethylene and acrylic acid.

### Experimental

**Materials.**—The vinylidene cyanide was prepared from di-(acetyl cyanide).<sup>16</sup> It was fractionally crystallized until it had a melting point no lower than 9.0°. The other monomers were commercial materials which were dried and fractionated. Special precaution was taken with the styrene and the vinyl ethers. The styrene was vacuum distilled under nitrogen and used fresh to avoid contamination with peroxides. Both the vinyl isobutyl ether and the vinyl butoxyethyl ether were washed three times with equal volumes of 1% NaOH, dried over CaH, refluxed over sodium for several hours, then fractionally distilled from the sodium. The benzene used was thiophene-free grade, dried over CaH, and then fractionated.

**Polymerizations.**—The experiments, except system 12, were run in thick-walled, 60-ml. Pyrex glass polymerization tubes with crown-cap closures (aluminum foil liners). The crown capped tubes were not suitable for system 12 due to the low boiling point of vinyl chloride monomer. All of the vinyl chloride polymerizations were run in small-necked glass polymerization tubes. The peroxide was added first; the tube was then evacuated and immersed in a Dry Ice-acetone-bath. The vinyl chloride was introduced into the evacuated tube. The vacuum was then broken and the vinylidene cyanide was added volumetrically. The tube was then sealed off with an oxygen-natural gas flame. The

(16) Ardis, *et al.*, *THIS JOURNAL*, **72**, 1305 (1950).

tubes in systems 1, 2, 3, 7, 8, 9, 11 and 15 were gassed with oil-pumped nitrogen; the others were not. They were all kept at constant temperature in water-baths controlled to  $\pm 0.1^\circ$ . The polymers were usually insoluble in the polymerization media. In the instances where the polymer was soluble, it was precipitated easily upon the addition of benzene. The only benzene-soluble polymer found is reported under system 16. It was isolated by low temperature evaporation of the benzene. The other polymers were all thoroughly washed with benzene and then vacuum dried to constant weight. All of the polymer analyses were run in duplicate—the nitrogen estimations by the semi-micro Kjeldahl method, the chlorine determinations by furnace combustion (A. S. T. M. method). The nitrogen values are accurate within 3 to 5 parts per thousand, *i.e.*,  $15.13 \pm 0.07\%$ . The chlorine values are a little less accurate due to the absence of a good method for the determination of the chlorine content of polymers. The determination of polymer composition by nitrogen analysis was particularly effective since in no instance did both monomers contain nitrogen. However, the analysis of polymers very high in vinylidene cyanide is less accurate because the nitrogen content of these samples changes with time of storage. Linkages of the type  $-\text{CH}_2-\text{C}(\text{CN})_2-\text{CH}_2-\text{C}(\text{CN})_2-$  are subject to scission by atmospheric moisture at room temperature. Each scission introduces a hydroxyl group on a chain end.<sup>2</sup>

The polymerization time required to achieve the desired low conversions ranged from 12 minutes to over 300 hours.

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## The Preparation of Acetylenic Ketones Using Soluble Silver Acetylides

By R. B. DAVIS AND D. H. SCHEIBER<sup>1</sup>

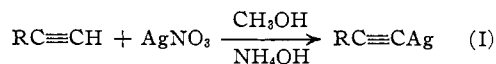
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Certain silver acetylides have been found to be soluble in such solvents as carbon tetrachloride, chloroform and benzene. The reaction of these silver acetylides in solution with acid halides yields  $\alpha,\beta$ -acetylenic ketones. By this method some new acetylenic ketones were prepared.

The formation of a precipitate in the presence of alcoholic or ammoniacal silver nitrate has long been used as a diagnostic test and a method of analysis<sup>2</sup> for compounds containing a terminal acetylenic group. The use of this reaction as a synthetic tool has been very limited, although utilized in the preparation of 1-halo derivatives.<sup>3</sup> Silver acetylides also have been employed catalytically in the preparation of acetylenic alcohols<sup>4</sup> and glycols.<sup>5</sup> In 1899, Nef<sup>6</sup> reported that propiolophenone could be produced by dissolving silver phenylacetylide in warm benzoyl chloride and boiling the resultant solution. However, the reaction was said to be quite violent and limited in its use to small quantities. Since that time there appears to be no mention in the literature of the use of silver acetylides

to synthesize ketones. One probable reason for the scant attention paid to these compounds is their low solubility in the media in which they are commonly prepared, although some are said to be somewhat soluble in hot alcohol.<sup>7</sup>

We have found that certain silver acetylides (I) dissolve in carbon tetrachloride, chloroform and



benzene. The solubility appears to depend on carbon content and also on the presence of other functional groups. Silver butylacetylide is soluble to the extent of at least two moles per liter in carbon tetrachloride.

Although the precipitate of white silver acetylide from ammoniacal silver nitrate and acetylene has been shown<sup>8</sup> to be  $\text{C}_2\text{Ag}_2$ , the composition of other silver acetylides appears to depend somewhat on

(1) Part of a Dissertation submitted by David H. Scheiber to the University of Notre Dame in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1956.

(2) Thomas L. Jacobs, "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 45.

(3) C. Liebermann, *Ann.*, **135**, 270 (1865).

(4) I. G. Farb., U. S. Patent 2,300,969; *C. A.*, **37**, 2014 (1943).

(5) I. G. Farb., German Patent 726,714; *C. A.*, **37**, 6274 (1943).

(6) J. U. Nef, *Ann.*, **308**, 277 (1899).

(7) P. Piganiol, "Acetylene, Homologs and Derivatives," Mapleton House, Brooklyn, N. Y., 1950, p. 276.

(8) *Inter alia*, L. Knorr and H. Mathes, *Ber.*, **32**, 736 (1899); J. Eggert and H. Shimank, *ibid.*, **51**, 454 (1918).