to a 55–45, weight per cent composition (53–47 mole per cent) of 2-carboxy-4,4′-dimethyldiphenyl sulfone and 2-carboxydiphenyl sulfone, respectively, according to the plotted data of Table I. Furthermore, a mixture melting point of 2-carboxy-4,4′-dimethyldiphenyl sulfone with the unknown mixture raised the melting point, while a mixture melting point of 2-carboxydiphenyl sulfone with the unknown mixture lowered the melting point, which information supports the composition designated from the plot. The above procedure was used by Truce and Norman[8] to determine the percentage composition of a mixture of isomeric carboxylic acids resulting from the metalation of 4-methyldiphenyl sulfone with *n*-butyllithium, followed by carbonation.

Determination of i factors. The diphenyl sulfone used was Eastman White Label sample recrystallized from benzene. The 4-*tert*-butyldiphenyl sulfone was prepared as described previously.[2] The 4-methyldiphenyl sulfone was prepared from *p*-toluenesulfonyl chloride and benzene in the presence of aluminum chloride. The product melted at 124–125° (reported[11] 125–125.5°). The apparatus, technique, and solvent for the cryoscopic measurements have been described previously.[15] The solvent was prepared with care so that the freezing point of the 100% sulfuric acid was on the linear portion on the water side of the freezing point-composition curve as shown by Gillespie.[16] The apparatus was allowed to stand several hours for the sulfuric acid to absorb the moisture from the air in the cell before the initial freezing point of the acid was determined. The supercooling of the solutions was controlled to ±0.1°. The solutions in the cryostat were held below 18° throughout the period in which freezing point measurements were being made.[17] For diphenyl sulfone, three independent runs gave *i* factors of 1.19, 1.20, and 1.17, calculated from freezing points taken 15 to 20 min. after addition of the sulfone to the cryostat. Single runs gave corresponding values of 1.20 for 4-methyldiphenyl sulfone, 1.26 for 4-*tert*-butyldiphenyl sulfone, and 1.81 for 4,4′-dimethyldiphenyl sulfone.

Determination of solubilities. Samples of diphenyl sulfone and 4,4′-dimethyldiphenyl sulfone were placed in dry ether which was then refluxed for a short time. The solutions were decanted into glass-stoppered Erlenmeyer flasks which were placed in a thermostat at 25 ± 0.02° and allowed to reach temperature equilibrium. The sulfones, in excess of the amount required to saturate the ether, precipitated during this period. Samples of the clear supernatant liquid were withdrawn into a gravimetric pipet, and 10 ml. of the saturated solutions delivered into a weighing bottle. The solvent was evaporated, and the weights of the sulfones determined gravimetrically. The Erlenmeyer flasks containing the solutions were then placed in an ice bath and allowed to stand until equilibrium conditions were reached. Samples of the saturated solutions were withdrawn and their sulfone content determined as before. The results of duplicate determinations expressed in moles per liter of solution are as follows:

Diphenyl sulfone	25°	.0830, .0829
	0°	.0400, .0396
4,4′-Dimethyldiphenyl sulfone	25°	.0436, .0443
	0°	.0207, .0208

Knoxville, Tenn.

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[15] C. M. Welch and H. A. Smith, *J. Am. Chem. Soc.*, **72**, 4748 (1950).

[16] R. J. Gillespie, *J. Chem. Soc.*, 2496 (1950).

[17] H. A. Smith and R. G. Thompson, *J. Am. Chem. Soc.*, **77**, 1778 (1955).

[Contribution from the Departments of Chemistry, University of Maryland and Wayne State University]

Pyrolysis of Esters. XI. A New Synthesis of α-Alkylacrylonitriles[1,2]

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Received March 15, 1957

The selectivity in the direction of elimination during the pyrolysis of tertiary esters has been used to prepare a series of α-alkylacrylonitriles. Thus α-ethyl-, α-*n*-propyl-, α-isobutyl-, and α-*n*-hexylacrylonitriles were prepared in 73 to 94% yields by the pyrolysis of the acetates derived from the corresponding methyl ketone cyanohydrins. Each of these monomers was polymerized by peroxide to a moderately high molecular weight polymer, with the poly-α-ethylacrylonitrile softening at 110–140°. One must conclude that previous preparations of these monomers were not free from inhibitors. These present results are additional evidence for the high degree of selectivity during the pyrolysis of esters.

Previous work in these laboratories has shown that the pyrolysis of esters proceeds in a highly selective manner to produce almost exclusively the least highly alkylated olefin according to the Hofmann rule.[6,7] For example, the pyrolysis of methylisopropylcarbinyl acetate gave almost exclusively 3-methyl-1-butene with little or no formation of the other possible isomer, 2-methyl-2-butene. It was shown that the presence of an unsaturated electron-withdrawing group in the β-position to the acyloxy group resulted in the formation of primarily the

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[1] Previous paper in this series, *J. Org. Chem.*, **21**, 858 (1956).

[2] (a) Presented in part before the Division of Polymer Chemistry at the 128th National Meeting of the American Chemical Society, Minneapolis, Minn., September 1955; (b) Abstracted in part from a dissertation submitted by John J. Hewitt to the Graduate Council of Wayne State University, December 1952, and from a thesis submitted by Floyd E. Naylor to the faculty of the Graduate School of the University of Maryland, December 1955, in partial fulfillment of the requirements of the degrees of Doctor of Philosophy.

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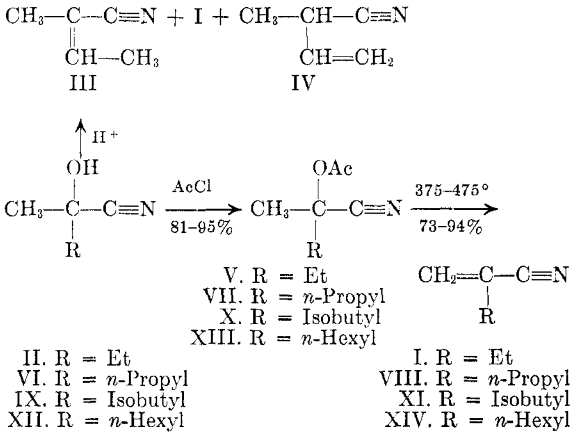
[4] Office of Naval Research Fellow, University of Maryland, 1951–1955.

[5] Research Corporation Fellow, Wayne State University, 1951–1952.

[6] W. J. Bailey and C. King, *J. Am. Chem. Soc.*, **77**, 75 (1955).

[7] W. J. Bailey, C. King, and J. J. Hewitt, *J. Am. Chem. Soc.*, **77**, 357 (1955).

conjugated isomer.[8] However, the presence of a β-methoxy or a β-dimethylamino group did not seem to affect either the selectivity or the direction of elimination.[9] It seemed very probable that this selectivity could be used for the synthesis of interesting monomers for polymerization that are either impossible or difficult to synthesize by conventional methods. Actually, since the discovery of the new heterogeneous catalysts for the polymerization of alpha olefins,[10] many uses of this method in the hydrocarbon field are quite obvious. For example, the pyrolysis of methylisobutylcarbinyl acetate to produce 4-methyl-1-pentene is certainly the method of choice for the synthesis of this alpha olefin.



Methacrylonitrile can be prepared conveniently by the dehydration of acetone cyanohydrin. However, the corresponding dehydration of methyl ethyl ketone cyanohydrin (II) produces a mixture containing as the main product β-methylcrotonitrile (III) plus only a small amount of α-ethylacrylonitrile (I). Furthermore, these two isomers apparently are difficult to separate by conventional distillation. Even though there are many reports of the synthesis of α-ethylacrylonitrile (I) and other α-alkyl derivatives,[11,12] there has been no report of a successful homopolymerization of any of these monomers. For these reasons, Marvel, Miller, and Chou developed a synthesis of I and other analogous α-alkylacrylonitriles from the corresponding α-alkylacroleins by dehydration of the corresponding oxime.[12] Even with this improved procedure they report,[13] ".... very little success was had in obtaining homopolymers from α-ethyl- or α-n-pentylacrylonitrile with either free-radical or ionic initiators." One of the explanations that has been advanced for the failure of I to homopolymerize has been the steric hindrance of the ethyl group. In view of the fact that α-methylacrylonitrile homopolymerizes very readily it did not seem reasonable that the introduction of a CH_2 group should stop homopolymerization completely. In fact an examination of the models of the two monomers and their polymers did not indicate that the steric effect should be highly pronounced. It seemed possible that the failure of the previous samples of I to homopolymerize might be due to the presence of small amounts of isomeric impurities, such as III or IV, that were formed during dehydration with an acid catalyst. Any of these impurities, especially IV, could act as a chain transfer agent and prevent the formation of a high polymer. This view is further strengthened by the fact that α-phenylacrylonitrile,[14] which cannot form such isomeric impurities, does indeed homopolymerize.

Since the pyrolysis of esters has been shown to proceed in a selective manner with simple compounds, it seemed possible that this method could be used to prepare α-ethylacrylonitrile (I) from the α-acetoxy-α-methylbutyronitrile (V). If the sample of I prepared in this manner could be made to homopolymerize, this would not only serve as additional evidence concerning the selectivity of the elimination reaction but would also disprove the hypothesis that steric hindrance prevented the homopolymerization in the previous examples.

For this reason the cyanohydrin of methyl ethyl ketone (II) was esterified with acetyl chloride to produce a 95% yield of V. The use of acetic anhydride resulted in recovery of starting material even after reflux for several days, and the use of pyridine with the acetyl chloride gave products that were difficult to purify. The tertiary acetate V was then dropped through a pyrolysis tube packed with $^{1}/_{8}$-inch borosilicate glass helices and externally heated at 475°. Conditions were carefully controlled in order that charring was virtually eliminated and that only 83% of the theoretical amount of acetic acid was liberated. Under these conditions a 73% yield of α-ethylacrylonitrile (I) was produced. Although the identity of this sample of I was established by agreement of its physical constants

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[8] W. J. Bailey and C. King, *J. Org. Chem.*, **21**, 858 (1956).

[9] W. J. Bailey and L. Nicholas, *J. Org. Chem.*, **21**, 648 (1956).

[10] G. Natta, *J. Polymer Sci.*, **16**, 143 (1955); G. Natta, P. Pino, G. Mazzanti, P. Corradini, and U. Giannini, *Rend. accad. nazl. Lincei*, [8] **18**, 19 (1955).

[11] (a) P. Bruylants, L. Ernould, and M. Dekoker, *Bull. sci. acad. roy. Belg.*, [5] **16**, 721 (1930); (b) M. Vossen, *Bull. soc. chim. Belg.*, **41**, 331 (1932); (c) A. Vermeulen and L. Adriaens, *Bull. soc. chim. Belg.*, **38**, 301 (1929); (d) A. Craen, *Bull. soc. chim. Belg.*, **42**, 410 (1933); (e) P. Ceuterick, *Bull. soc. chim. Belg.*, **44**, 89 (1935); (f) G. Verhulst and C. Glorieux, *Bull. soc. chim. Belg.*, **41**, 501 (1932).

[12] C. S. Marvel, W. R. Miller, and L. C. Chou, *J. Am. Chem. Soc.*, **72**, 5408 (1950).

[13] C. S. Marvel, R. T. Stiehl, W. K. Taft, and B. G. Labbe, *Ind. Eng. Chem.*, **46**, 804 (1954); a private communication from R. T. Stiehl indicated that during a distillation of α-ethylacrylonitrile a solid polymer accidentally resulted but that this polymer was not completely characterized.

[14] A. M. Clifford and J. R. Long, U. S. Patent **2,362,049** (1944); *Chem. Abstr.*, **39**, 2296 (1945).

with the reported values as well as by its infrared spectrum, the purity of I really was established by the fact that this monomer would homopolymerize. Thus when a benzene solution of I was heated with benzoyl peroxide, a solid poly-α-ethylacrylonitrile, softening point 110–140°, resulted. Although its intrinsic viscosity was only 0.12, this is the first solid homopolymer reported from this monomer. Even though these results seem to indicate that there may be some steric hindrance to polymerization in I, the effect is not nearly as large as previously believed. Furthermore, these results indicate that the previously prepared samples of I must have contained some impurity, such as III or IV, that could act as a chain transfer agent. These results also offer additional evidence of the high degree of selectivity of the elimination in the pyrolysis of esters, provided that any charring that could cause acid-catalyzed rearrangements is eliminated.

Chapin and Smith,[15] for example, carried out the pyrolysis of the α-acetoxy-α-methylbutyronitrile (V) over clay plate and obtained a sample of impure I that could not be homopolymerized or purified by distillation. They did establish the presence of the isomeric methylcrotonitrile III in their pyrolysis product. Apparently the clay plate was acidic enough to cause either some acid-catalyzed elimination of acetic acid from V or some acid-catalyzed rearrangement of the resulting olefin I.

In order to establish more clearly the extent of steric hindrance to polymerization it seemed of interest to prepare a series of alpha-substituted acrylonitriles. It was thought that, if several acrylonitriles with fairly large alpha substituents could be prepared and made to homopolymerize, one could conclude more definitely that steric hindrance could not completely account for the failure of previously prepared α-alkylacrylonitriles to polymerize. For this reason the syntheses of α-*n*-propyl-, α-isobutyl-, and α-*n*-hexylacrylonitriles (VIII, XI, XIV) were undertaken.

Methyl *n*-propyl ketone cyanohydrin (VI) was heated with acetyl chloride to produce a 93% yield of the corresponding acetate VII. Pyrolysis of VII at 385° with care to avoid carbonization produced a 55% conversion to α-*n*-propylacrylonitrile (VIII). Since 38% of the starting ester was recovered, the yield of VIII, based on unrecovered material, was 89%. When VIII was homopolymerized in a standard peroxide-catalyzed emulsion system, a white powdery poly-*n*-propylacrylonitrile, softening at 60–64° and having an intrinsic viscosity of 0.12, was obtained.

Similarly, methyl isobutyl ketone cyanohydrin (IX) was acetylated with acetic anhydride in an 81% yield and the resulting acetate X was pyrolyzed at 375° to produce a 46% conversion to α-isobutylacrylonitrile (XI). Since a 40% recovery of X also was obtained, the yield of XI, based on unrecovered material, was 77%. Standard emulsion polymerization of XI produced a solid white polymer, softening at 50–54° and having an intrinsic viscosity of 0.1.

Methyl *n*-hexyl ketone cyanohydrin (XII) was acetylated with acetyl chloride in a 90% yield and the resulting acetate XIII was pyrolyzed at 375° to yield a 48% conversion to α-*n*-hexylacrylonitrile (XIV). Again, since 49% of the starting ester XIII was recovered, the yield of XIV, based on unrecovered material, was 92%. Standard emulsion polymerization of XIV produced a viscous oil with an intrinsic viscosity of 0.11. The polymer, on cooling, formed a solid, softening point 15–18°.

The softening-point relationships in this series are approximately what one would expect from a series of amorphous polymers with increasing size of a side chain. Rehberg and Fisher[16] found that as one increased the number of carbon atoms in the alkyl group in a series of poly-*n*-alkyl methacrylates, the brittle point dropped from 88° for the methyl ester to $-35°$ for the dodecyl ester. (The *n*-amyl derivative softened at $+3°$.) Similarly, Overberger, Frazier, Mandelman, and Smith[17] found that, as the length of the side chain was increased in a series of poly-*p*-alkylstyrenes, the softening point dropped from 100° for polystyrene to about $-65°$ for the *n*-decyl derivative. (The *n*-hexyl derivative softened at $-27°$.)

In order to obtain some idea of the reactivity of one of these α-substituted acrylonitriles, a copolymerization was carried out with α-isobutylacrylonitrile (XI) and methyl methacrylate. The product, softening point 115–145°, intrinsic viscosity 0.3, obtained from a monomer mixture containing 40% by weight of the nitrile XI, after a 6% conversion, contained only 33% of XI.

Even though the molecular weights of the poly-α-alkylacrylonitriles were not extremely high, this is the first report of a solid homopolymer for this series. One would conclude, therefore, that steric hindrance to polymerization must be somewhat important but not enough to prevent homopolymerization. This steric effect probably exaggerated the effect of impurities on the polymerization. Thus chain transfer agents, such as III or IV, if present in previous preparations of these monomers, probably would have had a large inhibitory effect on the homopolymerization. Apparently the amount of these inhibitors in the monomers prepared by pyrolysis was not as large. One can conclude, therefore, that the pyrolysis of esters does indeed proceed in a highly selective manner and is an excellent method for the preparation of monomers for polymerization.

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(15) E. C. Chapin and R. F. Smith, *J. Am. Chem. Soc.*, **76**, 4179 (1954).

(16) C. E. Rehberg and C. H. Fisher, *Ind. Eng. Chem.*, **40**, 1429 (1948).

(17) C. G. Overberger, C. Frazier, J. Mandelman, and H. F. Smith, *J. Am. Chem. Soc.*, **75**, 3326 (1953).

EXPERIMENTAL[18]

Methyl ethyl ketone cyanohydrin (II). By a modification of the procedure for the preparation of acetone cyanohydrin,[19] 500 g. (9.7 moles) of powdered 95% sodium cyanide, 1.2 liters of water, and 887 g. (12.3 moles) of methyl ethyl ketone were placed in a 5-liter, three-necked flask equipped with a stirrer, a dropping funnel, and a thermometer. While the reaction mixture was maintained below 15°, 2.1 liters (8.5 moles) of 40% sulfuric acid was added with vigorous stirring over a 3-hr. period. After the organic layer was dried over anhydrous sodium sulfate, the excess methyl ethyl ketone was removed by distillation and the residue was fractionated through a 12-in., helix-packed column to yield 672 g. (80%) of methyl ethyl ketone cyanohydrin (II), b.p. 108.4° (40 mm.), n_D^{25} 1.4127, d_{25}^{25} 0.9212 [reported[15] b.p. 87–88° (17 mm.), n_D^{24} 1.4119].

Anal. Calcd. for C_5H_9NO: C, 60.58; H, 9.15. Found: C, 60.81; H, 9.37.

α-Acetoxy-α-methylbutyronitrile (V). To 99 g. (1 mole) of methyl ethyl ketone cyanohydrin (II) was added 79 g. (1 mole) of acetyl chloride at a rate slow enough to keep the temperature below 80°. After the reaction mixture had been heated for 12 hr., it was extracted with water, a saturated sodium carbonate solution, and again with water. The mixture was then dried over anhydrous sodium sulfate and fractionated through a 12-in., helix-packed column to yield 134 g. (95%) of α-acetoxy-α-methylbutyronitrile (V), b.p. 108–109° (40 mm.), n_D^{25} 1.4137, d_{25}^{25} 0.9808 [reported[15] b.p. 90–91° (16 mm.), n_D^{24} 1.4111].

Anal. Calcd. for $C_7H_{11}NO_2$: C, 59.55; H, 7.85. Found: C, 59.59; H, 7.70.

α-Ethylacrylonitrile (I). At the rate of 2 g. per min., 100 g. (0.71 mole) of α-acetoxy-α-methylbutyronitrile (V) was added dropwise through a vertical Vycor tube packed with 1/8-in. borosilicate glass helices and externally heated at 475°, as described previously.[20] The pyrolysate was condensed in a 6-inch spiral condenser and collected in a 300-ml., side-inlet flask cooled in a Dry Ice–chloroform–carbon tetrachloride bath. In order to prevent charring the apparatus was continuously flushed with a slow stream of oxygen-free nitrogen. The pyrolysate was extracted with water until the aqueous extracts tested neutral to litmus, and the organic layer was then dried over a mixture of anhydrous sodium sulfate and potassium carbonate. (Titration of an aliquot of the aqueous extracts with standard base indicated that 83% of the theoretical amount of acetic acid had been liberated.) Fractionation through a 6-in., helix-packed column produced 50 g. (73%) of α-ethylacrylonitrile (I), b.p. 112.5–113°, n_D^{25} 1.4120, d_{25}^{25} 0.8083 [reported[15] b.p. 111.9–112.9°, n_D^{20} 1.4118].

Anal. Calcd. for C_5H_7N: C, 74.03; H, 8.68. Found: C, 74.15; H, 8.71.

Polymerization of α-ethylacrylonitrile (I). A solution of 10 g. of α-ethylacrylonitrile (I) and 0.1 g. of benzoyl peroxide in 50 ml. of benzene was heated under reflux for 35 hr. The benzene solution was extracted with a dilute sodium hydroxide solution and then treated with Norite to remove a yellow color. Addition of an excess of petroleum ether produced a precipitate, which was removed by filtration and dried in vacuum to yield 6 g. of white poly-α-ethylacrylonitrile which began to shrink at 110° and completely softened below 140°. The polymer had an intrinsic viscosity of 0.12.

Anal. Calcd. for $(C_5H_7N)_x$: C, 74.03; H, 8.68. Found: C, 74.10; H, 8.49.

α-Acetoxy-α-methylvaleronitrile (VII). Methyl *n*-propyl ketone cyanohydrin (VI), b.p. 101° (17 mm.), n_D^{25} 1.4200 [reported[21] b.p. 100° (21 mm.), n_D^{19} 1.42065], was prepared in a 76% yield by a modification of the procedure described above for methyl ethyl ketone cyanohydrin (II). To 160 g. (1.5 moles) of the cyanohydrin VI, heated in a 500-ml., three-necked flask fitted with a dropping funnel and a reflux condenser protected with a calcium chloride tube, was added dropwise 120 g. (1.5 moles) of acetyl chloride over a 1-hr. period. After the reaction mixture had been heated under reflux for 14 hr., it was fractionated through a 10-in., helix-packed column to yield 221 g. (93%) of α-acetoxy-α-methylvaleronitrile (VII), b.p. 96° (25 mm.), n_D^{25} 1.4186.

Anal. Calcd. for $C_8H_{11}NO_2$: C, 61.93; H, 8.38. Found: C, 61.86; H, 8.25.

α-n-Propylacrylonitrile (VIII). At the rate of 3 g. per minute, 71.5 g. (0.46 mole) of α-acetoxy-α-methylvaleronitrile (VII) was added dropwise through the same pyrolysis tube described above heated at 385°. The same procedure for the pyrolysis and treatment of the pyrolysate also was used with the exception that the pyrolysate was dissolved in 50 ml. of ether before extraction. (Titration of an aliquot of the aqueous extracts indicated that 55% of the theoretical amount of acetic acid had been liberated.) Distillation of the ether solution through a 10-inch, helix-packed column yielded 39 g. (55%) of α-*n*-propylacrylonitrile (VIII), b.p. 134° (760 mm.), n_D^{25} 1.4211 [reported[11c] b.p. 135.7° (757 mm.), n_D^{20} 1.42283], and 27.5 g. (38% recovery) of the starting acetate VII. The yield of VIII, based on unrecovered VII, was, therefore, 89%.

Anal. Calcd. for C_6H_9N: C, 75.79; H, 9.47. Found: C, 75.56; H, 9.57.

Polymerization of α-n-propylacrylonitrile (VIII). In a 2-oz. vial were placed 5.5 g. (0.058 mole) of α-*n*-propylacrylonitrile (VIII), 18 g. of water, 0.02 g. of potassium persulfate, 0.03 g. of lauryl mercaptan, and 0.5 g. of sodium stearate and the vial was carefully flushed with nitrogen. The vial was rotated end-over-end at 50° for 5 days. Additional potassium persulfate was added at 24-hr. intervals. The polymer emulsion was poured into 100 ml. of vigorously stirred methanol. After the resulting precipitate was removed by filtration, it was redissolved in 10 ml. of tetrahydrofuran and reprecipitated by the addition of this solution to an additional 100 ml. of methanol. The precipitate was removed by filtration and dried under vacuum to yield 0.9 g. (17% conversion) of a white powder of poly-α-*n*-propyl acrylonitrile, softening point 60–64°, $[\eta]_{C \to O}$ 0.12.

α-Acetoxy-α,γ-dimethylvaleronitrile (X). Methyl isobutyl ketone cyanohydrin (IX), b.p. 109° (24 mm.), n_D^{25} 1.4240 [reported[22] b.p. 109° (24 mm.), n_D^{21} 1.42595], was prepared in a 78% yield by a modification of the procedure described above for methyl ethyl ketone cyanohydrin (II). In a 1-l., 3-necked flask fitted with two reflux condensers were placed 127 g. (1 mole) of the cyanohydrin IX, 408 g. (4 moles) of acetic anhydride and 60 g. of acetic acid. After the reaction mixture had been heated under reflux for 72 hr., it was fractionally distilled through a 10-in., helix-packed column to yield 137 g. (81%) of α-acetoxy-α,γ-dimethylvaleronitrile (X), b.p. 125° (36 mm.), n_D^{25} 1.4220.

Anal. Calcd. for $C_9H_{15}NO_2$: C, 63.87; H, 8.92. Found: C, 63.78; H, 8.75.

α-Isobutylacrylonitrile (XI). At the rate of 3 g. per min.,

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[18] The authors are grateful to Dr. Mary Aldridge, Kathryn Gerdeman, and Vivian Kapuscinski for the microanalyses and to Dr. Robert A. Spurr and Dr. Joseph Wenograd for the infrared absorption spectra. The infrared spectra were determined on the pure liquids with a Perkin-Elmer model 12-C spectrometer modified for double-pass operation. The authors also are grateful to Joseph Antonucci, Robert Barclay, Jr., and William Graham Carpenter for the preparation of methyl propyl ketone cyanohydrin (VI), methyl isobutyl ketone cyanohydrin (IX), and methyl *n*-hexyl ketone cyanohydrin (XII), respectively.

(19) R. F. B. Cox and R. T. Stormont, *Org. Syntheses*, **Coll. Vol. II**, 7, (1946).

(20) W. J. Bailey and J. J. Hewitt, *J. Org. Chem.*, 21, 543 (1956).

(21) A. Lapworth and R. H. F. Manske, *J. Chem. Soc.*, 2548 (1928).

(22) A. J. Ultee, *Rec. trav. chim.*, **28**, 7 (1909).

85 g. (0.5 mole) of α-acetoxy-α,γ-dimethylvaleronitrile (X) was added dropwise to the pyrolysis tube heated at 375°. The pyrolysate was worked up as indicated previously for that from the pyrolysis of VII. (Titration of an aliquot of the aqueous extracts indicated that 55% of the theoretical amount of acetic acid had been liberated.) The ether extract was fractionally distilled through a 10-in., helix-packed column to yield 25 g. (46%) of α-isobutylacrylonitrile (XI), b.p. 68° (50 mm.), n_D^{25} 1.4232, and 33 g. of the starting acetate X. The yield of XI, based on unrecovered starting material, was 77%.

Anal. Calcd. for $C_7H_{11}N$: C, 77.06; H, 10.09. Found: C, 77.08; H, 9.85.

Polymerization of α-isobutylacrylonitrile (XI). By the use of a procedure similar to that described for α-*n*-propylacrylonitrile (VIII), 4 g. of α-isobutylacrylonitrile (XI) was polymerized in an emulsion system over a 4-day period. The crude polymer, formed by coagulation in methanol, was redissolved in tetrahydrofuran and was then reprecipitated by the addition of this solution to methanol. The white powder was dried under vacuum to yield 0.4 g. (10%) of poly-α-isobutylacrylonitrile, softening point 50–54°, $[\eta]_{c\to 0}$ 0.1.

Copolymerization of α-isobutylacrylonitrile (XI) *and methyl methacrylate.* By a procedure similar to that described for the polymerization of α-*n*-propylacrylonitrile (VIII), 2 g. of α-isobutylacrylonitrile and 3 g. of methyl methacrylate were copolymerized over a 52-hr. period. The emulsion was poured into 200 ml. of methanol and the mixture was made acidic to litmus. After the copolymer was collected by filtration, it was redissolved in 10 ml. of tetrahydrofuran and reprecipitated by the addition of this solution to 100 ml. of methanol. The copolymer was dried under vacuum to yield 0.3 g. of a white powder, softening point 115–145°, $[\eta]_{c\to 0}$ 0.3. Analysis showed that the copolymer contained 3.97% nitrogen, which indicated that the copolymer contained approximately 1 mole of α-isobutylacrylonitrile for every 2 moles of methyl methacrylate.

α-Acetoxy-α-methylcaprylonitrile (XIII). Methyl *n*-hexyl ketone cyanohydrin (XII), b.p. 130° (11 mm.), n_D^{25} 1.4301 [reported[11f] b.p. 131–132° (11 mm.), n_D^{20} 1.43227], was prepared in a 58% yield by a modification of the procedure described above for the preparation of methyl ethyl ketone cyanohydrin (II). By the same procedure described above for the preparation of α-acetoxy-α-methylvaleronitrile (VII), 90 g. (0.58 mole) of the cyanohydrin XII was acetylated with 70 g. (0.89 mole) of acetyl chloride to yield 100 g. (90%) of α-acetoxy-α-methylcaprylonitrile (XIII), b.p. 128° (12 mm.), n_D^{25} 1.4286.

Anal. Calcd. for $C_{11}H_{19}NO_2$: C, 67.01; H, 9.65. Found: C, 66.99; H, 9.38.

α-n-Hexylacrylonitrile (XIV). At the rate of 3 g. per min., 71 g. (0.38 mole) of α-acetoxy-α-methylcaprylonitrile (XIII) was added dropwise to the pyrolysis tube heated at 375°,as described above. The pyrolysate was worked up as described for the *n*-propylacrylonitrile (VIII). (Titration of an aliquot of the aqueous extracts indicated that 48% of the theoretical amount of acetic acid had been liberated.) The ether extract was fractionally distilled through a 10-in., helix-packed column to yield 24.5 g. (48%) of α-*n*-hexylacrylonitrile (XIV), b.p. 114° (50 mm.), n_D^{25} 1.4347 [reported b.p. 80° (12 mm.),[11f] b.p. 201° (766 mm.),[11f] b.p. 112° (48 mm.),[12] n_D^{20} 1.43972,[11f] n_D^{20} 1.4350[12]], and 35 g. of the starting acetate XIII. The yield of XIV, based on unrecovered starting material, was 92%.

Anal. Calcd. for $C_9H_{15}N$: C, 78.83; H, 10.95. Found: C, 79.11; H, 10.71.

Polymerization of α-n-hexylacrylonitrile (XIV). By a procedure very similar to that described for α-*n*-propylacrylonitrile (VIII), 5 g. (0.036 mole) of α-*n*-hexylacrylonitrile (XIV) was polymerized in an emulsion system over a 4-day period. The polymer was purified as described above to yield 0.3 g. of a clear viscous poly-α-*n*-hexylacrylonitrile, $[\eta]_{c\to 0}$ 0.11, which became a hard glass at 0° and resoftened at 15–18°.

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[CONTRIBUTION FROM THE SOUTHERN REGIONAL RESEARCH LABORATORY[1]]

Kinetics of Diels-Alder Reactions of Eleostearic Acids with Maleic Anhydride and Substituted Maleic Anhydrides

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Received April 26, 1957

The kinetics of the Diels-Alder reactions of *alpha*- and *beta*-eleostearic acids with chloromaleic, methylmaleic, and maleic anhydrides have been investigated. The reactions of chloromaleic anhydride and maleic anhydride with the eleostearic acids conformed to second order kinetics, but those of methylmaleic anhydride particularly with *alpha*-eleostearic acid, were not strictly second order. The specific rate constants for the Diels-Alder reactions of *beta*-eleostearic acid were found to be of greater magnitude than those for *alpha*-eleostearic acid, and the reactions of the former were found to be less temperature-dependent than the reactions of the latter. Energies of activation for the systems in which *beta*-eleostearic acid was a reactant were markedly lower than those for systems containing *alpha*-eleostearic acid, while the magnitude of the frequency factors of the respective systems was reversed. Substitution of either a methyl group or chlorine atom into maleic anhydride resulted in diminished dienophilic activity. The influences of structure, steric requirements, and group inductive effects on the specific rate constants of the various reactions have been considered.

In continuing the study of the Diels-Alder reactions of *alpha*- and *beta*-eleostearic (octadecatrienoic) acids[2,3] we have now investigated the kinetics of their reactions with maleic anhydride, chloromaleic anhydride, and methylmaleic anhydride (citraconic anhydride). This series of dienophiles

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