Preparation of oxetanes. General method. Potassium and sodium hydroxide were powdered and a mixture of equal weights of the two was prepared. For preparation of the oxetane, one part of the ditosylate was intimately mixed with two to three parts of the potassium–sodium hydroxide mixture and placed in a round bottom, single-neck flask of adequate capacity. (Some swelling of the mixture occurs on heating.) The mixture of materials was heated in a high vacuum to a temperature of 300–400°. The gaseous products were trapped in a Dry Ice–cooled flask followed by a Dry Ice–cooled trap. When no more material appeared to be coming out of the frothing mixture, the distillation was stopped and the traps were allowed to warm to room temperature. A mixture of two liquids was obtained, the bottom layer consisting of water and the top layer consisting of the desired organic material contaminated with by-products. The organic layer was separated, washed with water, and dried, then distilled through a spinning band column. Properties of the oxetanes are shown in Table III. These oxetanes are shown in Table III. These oxetanes are rather prone to autoxidation and should be protected from oxygen. All of them showed the characteristic oxetane infrared band at *ca.* 10.2 μ.[8]

Polymerization of oxetanes. General method. Two to five grams of pure monomer was placed in a 100-ml., three-necked flask equipped with a stirrer, a gas inlet, and a Dry Ice condenser, and maintained under an atmosphere of nitrogen. From a cylinder about 50 ml. of methyl chloride was condensed into the flask which was cooled in a Dry Ice bath. The methyl chloride cylinder was detached and the contents of the flask stirred and refluxed (−25°) gently. To the reaction vessel was now connected a small tube containing 1–2 g. of *p*-chlorobenzenediazonium hexafluorophosphate[19] by means of a short length of tubing. A stream of nitrogen was passed through the tube containing the diazonium salt into the reaction vessel. The diazonium salt was heated in an oil bath to about 150°–160° to cause evolution of phosphorus pentafluoride, which was swept with the nitrogen stream into the reaction vessel. Polymerization of the oxetane usually occurred within a very short time if the monomer was of a high degree of purity. The polymer separated from the methyl chloride either as a white powder or as a swollen mass similar in appearance to cottage cheese. The polymerization was exothermic and vigorous boiling of the methyl chloride occurred. After a few minutes a small amount of methyl alcohol was added to inactivate the catalyst. The methyl chloride was allowed to evaporate, and the solid residue consisting of polyether was separated, washed, and dried. Polymers were extracted with ether and alcohol, to remove traces of low molecular weight materials. No crystalline oligomers could be detected. The yield was usually quantitative. In all cases studied it was possible to prepare film by melt-pressing the polymer. However, only the products from the cyclohexene and the cyclohexane derivatives were sufficiently high in molecular weight to allow drawing and orientation studies. The others were too brittle to draw. Crystalline melting points were determined in the usual way on a Kofler hot stage between crossed polaroids. Data are collected in Table IV.

Residual unsaturation in polymers from unsaturated monomers was checked by infrared and bromine addition. It was assumed that no rearrangement of the carbon skeleton had occurred.

Preparation and polymerization of 7-oxaspiro[3.2]hexane. The monomeric compound (b.p. 103°/760 mm.) was prepared according to Searles and Lutz[11] from bis(chloromethyl)oxetane. This monomer, polymerized as above with phosphorus pentafluoride, gave a solid, crystallizable polymer with a crystalline m.p. of 45°. X-ray showed high crystallinity and high perfection.

Copolymer from bis(chloromethyl)oxetane and 2-oxa-7-methyl-Δ^6-spirononene. A mixture of 26.6 g. of freshly distilled 3,3-bis(chloromethyl)oxetane and 1.4 g. of freshly distilled 2-oxa-7-methyl-Δ^6-spirononene was polymerized in 250 ml. boiling methyl chloride in the usual manner with phosphorus pentafluoride. Vigorous boiling occurred when the catalyst was introduced in the reaction mixture, and the solution turned yellow. Polymer separated immediately. After evaporation of the solvent the polymer was washed with alcohol, which removed the yellow color; it was subsequently dried in a vacuum oven at 80°. The yield of the white finely divided polymer was 24 g. A clear, waxy film was pressed at 180° from the dry polymer. Strips of this film could be hand-drawn at room temperature *ca.* 6X. After boil-off in acetone, taut for 30 min., relaxed 5 min., the crystalline m.p. was 159–160°. X-ray diagram of such a strip showed the polymer to have high crystallinity and very high orientation.

Anal. Calcd. for $(C_5H_8OCl_2)_n$: C, 38.7; H, 5.2; Cl, 45.7. Calcd. for $(C_9H_{14}O)_n$: C, 77.4; H, 9.7; Cl, 0.0. Calcd. for 17:1 copolymer: C, 40.6; H, 5.4; Cl, 43.6. Found: C, 40.7, 40.9; H, 5.5, 5.6; Cl, 44.1, 44.3.

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(19) This compound is sold by the Ozark-Mahoning Co. under the tradename of "Phosfluogen A."

[CONTRIBUTION FROM THE MARSHALL LABORATORY, E. I. DU PONT DE NEMOURS AND CO.]

Transannular Polymerization of 2-Carbethoxybicyclo[2.2.1]-2,5-heptadiene

P. J. GRAHAM, E. L. BUHLE, AND N. PAPPAS

Received December 28, 1960

2-Carbethoxybicyclo[2.2.1]-2,5-heptadiene (I) has been polymerized to a high molecular weight, soluble polymer believed to contain nortricyclene repeating units. Attempted polymerizations of structures similar to I suggest that this type of transannular polymerization of bicycloheptadienes requires activation of the double bonds and resonance stabilization of radicals formed during the polymerization.

The polymerizability of 2-substituted bicyclo[2.2.1]-2,5-heptadienes has not been studied and little has been reported on the structure and properties of polymers of closely related bicycloheptadienes.[1-3] It has been found[4] that 2-carbethoxybicyclo[2.2.1]-2,5-heptadiene, I, polymerizes readily with free radical catalysts to give high molecular

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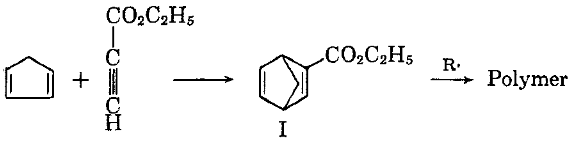
(1) A. A. Petrov and N. P. Sopov, *Zhur. Obshchei Khim,* **23**, 1034–1038 (1953).

weight, soluble, essentially saturated polymer. For example, polymers prepared with azodiisobutyronitrile had inherent viscosities from 0.45 to 0.71 in 0.1% benzene solution corresponding to molecular weights of 66,000 and 123,000, respectively, by osmotic pressure measurements.

I was prepared from cyclopentadiene and ethyl propiolate. Polymerizations of I were carried out at 60° in 50% benzene solution with 0.2% azodiisobutyronitrile (Table I). The polymer was precipitated in methanol giving 40–60% yields of polymer. Higher conversions usually resulted in some insoluble polymer.



Other initiator systems such as benzoin and ultraviolet light, peroxides, and coordination catalysts gave polymers which had identical infrared spectra and were presumably of identical structure.

TABLE I[a]

POLYMERIZATION OF I

Polymerization Solvent	Polymerization Time, Hr.	Yield of Polymer, %	Inherent Viscosity
Benzene	18	40	1.32[b]
Benzene	66	40	1.32[c]
Benzene	24	47	1.57[c]
t-Butyl alcohol	18	60	1.92[b]
Toluene	18	47	0.21[b]
No solvent	18	51	Gelled[d]

[a] Polymerizations were carried out with 0.2% of azodiisobutyronitrile at 60° in 50% solutions of the solvents given. [b] Inherent viscosity was determined in 0.1% benzene solution at 25°. [c] Inherent viscosity was determined in 0.1% dichloromethane at 25°. [d] Mostly insoluble polymer obtained.

Unlike the polymerization of methacrylates and other vinyl type monomers,[5] bulk polymerization of I was uninhibited by oxygen. As determined by time to reach a no flow point, I polymerizes more rapidly in the presence of air than under nitrogen (see Table II).

TABLE II

BULK POLYMERIZATION[a] OF I UNDER N_2 AND UNDER AIR

Monomer	Time to Reach No Flow Point, Minutes: Under N_2	Under air
2-Carbethoxybicyclo[2.2.1]-2,5-heptadiene (I)	276	163[b]
Butyl methacrylate	92	No apparent polymerization

[a] Polymerizations carried out at 60 ± 2° with 1% azodiisobutyronitrile. [b] The structure and properties of polymer from I obtained under air were not investigated.

The outstanding physical characteristic of polymer from I is its high modulus transition temperature (*tg* = 220°) which suggests a rigid polymer structure (see Table II). Films of the polymer embrittle slowly at 150° in the presence of air, and more rapidly at 250° to form dark, insoluble film. Analysis of the polymer treated in this manner shows an increase in oxygen content suggesting reaction with atmospheric oxygen. When heated similarly under nitrogen, the polymer yellows only slightly and remains soluble. The polymer is unaffected by treatment with 1*N* sodium hydroxide solution and dilute hydrochloric acid but dissolves slowly in alcoholic sodium hydroxide solution. An acetone solution of the polymer is unreactive to potassium permanganate reagent indicating it to be essentially saturated.

TABLE III

PROPERTIES OF POLYMER FROM I, M_n = 220,000

% Elongation to break	6
Tensile strength, lbs./in.^{2}	4600
Hardness, Knoop	7.3
Crystallinity (x-ray)	None
Tg	220
Tack T	295
Molding T (compression)	270
Thermal stability	Yellows; crosslinks above 150°
Solubility	Soluble in aromatic solvents, acetone, chloroform, methylene chloride, etc.

Polymer structure. The structure of polymer from I was investigated. In work to be reported, assignments will be suggested for the double bond absorptions of I in the infrared. These absorptions include the conjugated double bond stretching absorption at 6.23 μ, the unconjugated double bond stretching absorption at 6.40 μ, the conjugated vinyl C—H deformation at 13.15 μ and the unconjugated vinyl C—H deformation at 14.40 μ.[6] The infrared spectrum of a polymer prepared from I with azodiisobutyronitrile is shown in Fig. 1. The spectrum shows no absorption for vinyl stretching at 6.2–6.5 μ and no absorption at 14.4 μ. An absorption band of low intensity is present at 13.15 μ; however, it is unlikely that it is due to conjugated vinyl C—H de-

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(2) J. Hyman and Company, French Pat. 1,059,759, March 29, 1954.

(3) Arvey Corp., British Pat. 701,211, December 23, 1953.

(4) The polymerization of I was first observed by H. N. Cripps of the Central Research Department of E. I. du Pont de Nemours and Co.

(5) C. C. Price and C. E. Adams, *J. Am. Chem. Soc.*, **67**, 1674 (1945); I. M. Kolthoff and W. S. Dale, *J. Am. Chem. Soc.*, **69**, 441 (1947); **67**, 672 (1945); C. E. Barnes, *J. Am. Chem. Soc.*, **67**, 217 (1945).

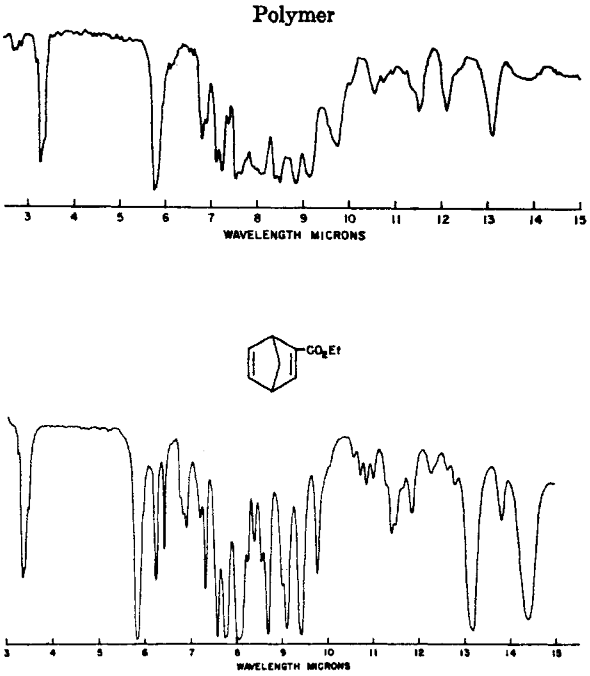
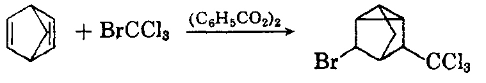


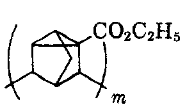
Figure 1

formation since the spectrum shows no absorption at 6.2–6.5 μ. This band is probably due to some other grouping in the polymer. Although both double bonds have disappeared during polymerization, absorption is still present at 3.25 μ. Since cyclopropane C—H reportedly[6,7] absorbs here, this band may be due to a cyclopropane ring C—H. The polymer also absorbs at 9.8 μ and 11.62 μ which are in the regions reported for cyclopropane ring absorption[8] and at 12.1 μ which is in the region reported[9] for nortricyclene rings.

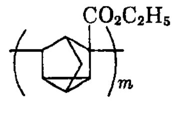
In ionic addition reactions, bicyclo[2.2.1]-2,5-heptadiene II, has been shown to add reagents such as hydrogen bromide,[10] bromine,[11] and RCOOH[12] in a 1,4-fashion to give nortricyclenes. In the free radical addition of trichlorobromomethane in the presence of benzoyl peroxide to II, the nortricyclene product also results indicating that free radicals also add 1,4 to the bicycloheptadiene ring system.[13]



The polymerization of I to give essentially saturated, soluble polymer, infrared data on the polymer, and the known chemistry of bicycloheptadienes, all suggest the polymers from I consist primarily of nortricyclene repeating units, III and IV.

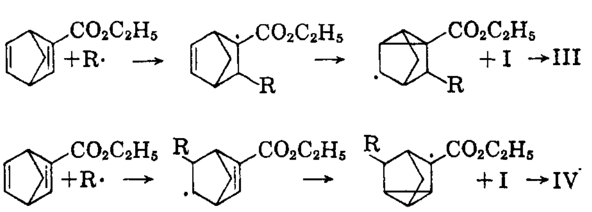


III



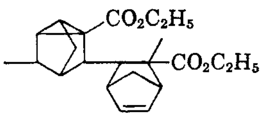
IV

III and IV could result in the following manner:



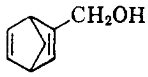
Hart and Mantin[14] have reported bands at 11.6–11.9 μ and 12.7–12.75 μ for 1-substituted nortricyclenes. Although the infrared spectra of polymers (Fig. 1) from I have bands close to these regions, they do not have bands in these regions. This suggests that if III is a repeating unit the bands expected in these regions have been shifted because of the additional substitution on the ring.

Some "1,2" polymerization may also occur to give an unsaturated polymer segment as follows:

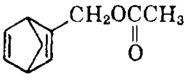


The unsaturation in these segments might explain our inability to achieve higher than 60% conversion without gelation and the apparent oxidative degradation of the polymer at elevated temperatures. This instability may also be due, however, to the nortricyclene ring system itself.

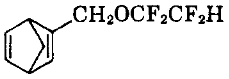
Several bicycloheptadienes (V–IX) were synthesized for polymerization studies.



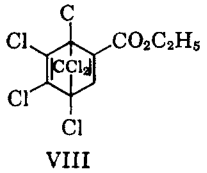
V



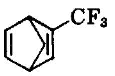
VI



VII



VIII



IX

V was prepared from propargyl alcohol and cyclopentadiene and converted to VI with acetyl chloride and to VII with tetrafluoroethylene and sodium. VIII was prepared from ethyl propiolate and

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(6) E. R. H. Jones, G. H. Mansfield, and M. C. Whiting, *J. Chem. Soc.*, 4073 (1956).

(7) J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, **73**, 5030 (1951).

(8) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Methuen and Co., London, 1954, p. 27–28.

(9) J. D. Roberts *et al.*, *J. Am. Chem. Soc.*, **72**, 3116 (1950).

(10) H. Bluestone, S. D. Soloway, J. Hyman, and R. E. Lidov, U. S. Pat. 2,730,548, Jan. 10, 1956.

(11) S. Winstein and M. Shatavsky, *Chem. & Ind.*, 56 (1956).

(12) H. Bluestone, S. D. Soloway, J. Hyman, and R. E. Lidov, U. S. Pat. 2,738,356, March 13, 1956.

(13) *Chem. Eng. News*, **35**, No. 7, 23, Feb. 18, 1957.

(14) H. Hart and R. A. Mantin, *J. Org. Chem.*, **24**, 1267 (1959).

TABLE IV

POLYMERIZATION OF BICYCLO[2.2.1]-2,5-HEPTADIENE (II)

Solvent	Catalyst	Polymerization Temperature	Polymerization Time, Hours	Polymer Yield	Inherent Viscosity[a] of Polymer
Benzene	0.2% Azodiisobutyronitrile	60	18	0	—
t-Butyl alcohol	0.2% Azodiisobutyronitrile	70	24	1	0.03
No solvent	1% Benzoin + U.V. light	25	24	0	—
No solvent	2% Ditertiary butyl peroxide	130	16	71	Gelled
t-Butyl alcohol	2% Ditertiary butyl peroxide	130	16	31	Gelled
t-Butyl alcohol	0.5% Ditertiary butyl peroxide	130	16	9	0.18
t-Butyl alcohol	0.2% Ditertiary butyl	130	16	4	0.10

[a] Inherent viscosities determined in 0.1% dichloromethane solution at 25°.

hexachlorocyclopentadiene, and IX was obtained from trifluoromethyl acetylene and cyclopentadiene.

Attempts to polymerize bicyclo[2.2.1]-2,5-heptadiene, II, under the same conditions employed for I resulted in very low yields of polymer (Table III). Under more severe polymerization conditions, II gave insoluble polymer. Attempted polymerization of V, VI, VII and VIII gave no detectable amount of polymer (Table IV). Polymerization of IX gave a low yield (< 3%) of a high melting solid containing fluorine which may be a polymer of IX.

TABLE V

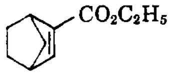
ATTEMPTED POLYMERIZATION OF V, VI, VII, AND VIII

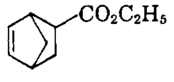
Monomer	Catalyst	Time of Polymerization, Hours	Result
V	Benzoin/U.V.[a]	24	No polymerization
VI	Benzoin/U.V.[a]	24	No polymerization
VII	Benzoin/U.V.[a]	24	No polymerization
VIII	Benzoin/U.V.[a]	24	No polymerization
V	Ditertiarybutyl Peroxide[b]	6	No polymerization

[a] 1% benzoin on the monomer was used. An AH-3 sunlamp was used, and the samples were placed in quartz tubes. [b] The polymerization was carried out at 135°.

From a comparison of structures II and V–IX with I, it appears that the ready polymerization of bicyclopentadienes requires a substituent to activate one of the double bonds and provide resonance stabilization of radicals formed during the polymerization. Inertness of VIII to polymerization may be due to steric factors and the inactivity of the ClC═CCl bond.

Two bicycloheptanes, 2-carbethoxybicyclo[2.2.1]-2-heptene, X, and 2-carbethoxybicyclo[2.2.1]-5-heptene, XI, will be reported. These compounds do not undergo vinyl polymerization with free radical catalysts under conditions used for I. Homopolymer of bicycloheptene (XII) with coordination catalysts has been reported to have a structure consisting of repeating vinyl cyclopentane groups.[15] Copolymers of XII have also been reported.[10] However, the relative inertness of these compounds to polymerization contrasts with the reactivity of I. Possibly, the bicycloheptadiene ring system requires a lower energy of activation for polymerization than do the bicycloheptene systems because of greater ring strain.


X


XI


XII

EXPERIMENTAL

All distillations were carried out in a 6 in. vacuum-jacketed Vigreux column unless otherwise stated. Infrared spectra were obtained with a Perkin-Elmer Model 21 spectrophotometer.

2-Carbethoxy[2.2.1]-2,5-heptadiene (I). Freshly distilled cyclopentadiene (66 g., 1.0 mole) was added to 80 g. (0.82 mole) of ethyl propiolate containing 10 mg. of hydroquinone. The reaction mixture was heated to 110°, then cooled to 60°, and fitted with a 5-in. column packed with Pyrex rings on top of which was placed a 6-in. vacuum-jacketed Vigreux column. Unchanged ethyl propiolate and cyclopentadiene were removed under reduced pressure, and the remaining mixture was distilled at 5 mm. pressure giving 20 g. of forerun at 47–80° and 79.5 g. (59% yield) of the desired product at 84°/5 mm., n_D^{25} 1.4853.

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37; ester equiv., 164.2. Found: C, 73.92, 73.94; H, 7.81, 7.83; ester equiv., 166, 168.

Polymerization of I *with azodiisobutyronitrile.* Polymers of I with molecular weight greater than 100,000 were obtained by heating the monomer in 50% benzene or *t*-butyl alcohol solution at 60° for 24 hr. under nitrogen with 0.2% azodiisobutyronitrile initiator. The polymer was isolated by precipitation in methanol in a Waring Blendor. The finely divided polymer was freed of monomer by washing with methanol until

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(15) W. L. Truett, D. R. Johnson, I. M. Robinson, and B. A. Montague, *J. Am. Chem. Soc.*, **82**, 2337 (1960).

all trace of monomer odor was gone. It was then dried in a vacuum oven at 50° for 24 hr.

Anal. Calcd. for $(C_{10}H_{12}O_2)$: C, 73.14; H, 7.37; O, 19.49. Found: C, 73.53; H, 7.46; O, 19.19.

Polymerization of bicyclo[2.2.1]-2,5-heptadiene (II). Low temperature (25–70°) polymerizations of II were carried out essentially as described for I (Table IV); polymerizations at 130° were done in an autoclave. The resulting solutions were added to methanol to precipitate any polymer formed.

Polymerization of I *with 1:1 vanadium oxytrichloride-titanium chloride and aluminum isobutyl.* A solution of 10 g. of I in 10 ml. of ethyl acetate was catalyzed with 0.06 ml. of 1:1 vanadium oxytrichloride–titanium tetrachloride (0.06 mmole) and 0.3 ml. of aluminum isobutyl (0.3 mmole) and stirred at room temperature for 24 hr. The resulting solution was added to 250 ml. of methanol giving 3.1 g. of polymer having an inherent viscosity of 0.25 in 0.1% benzene solution at 25°. The infrared spectrum of the polymer was essentially the same as polymers prepared with free radical catalysts.

Heating polymers from I *in the presence of air.* Films of approximately 2 mils thickness on glass panels heated for 23 hr. at 250° in the presence of air showed absorption of oxygen according to elemental analysis.

Analysis of polymer prior to heating.

Anal. Calcd. for $(C_{10}H_{12}O_2)_m$: C, 73.14; H, 7.37; O, 19.49. Found: C, 73.53; H, 7.46; O, 19.19.

Analysis of thermally treated polymer. Found: C, 67.29; H, 5.59; O, 25.55.

2-Methylolbicyclo[2.2.1]-2,5-heptadiene (V). V has been reported previously by another route.[2] In our case, a mixture of 200 g. (3.57 moles) of propargyl alcohol, 267 g. (2.0 moles) of dicyclopentadiene, and 5 g. of hydroquinone was heated at 200° for 3 hr. in an autoclave. The reaction mixture was distilled to give 145 g. of crude product, b.p. 78–104°/8 mm.; refractionated to give 102 g. (yield 25%) of the desired product, b.p. 100–103°/9–11 mm., n_D^{25} 1.5066–1.5073, λ_{max}^{liquid} 3.0 μ (OH); 6.13 μ and 6.41 μ (C=C).

Anal. Calcd. Hydroxyl number: 122.2. Found: 124 and 125.

Tetrafluoroethyl ether of V, VII. VII was prepared by D. C. England at the Central Research Department of the E. I. du Pont de Nemours and Co., by a procedure previously described.[16] The product was obtained in 50% yield, b.p. 75°/2 mm., n_D^{25} 1.4110.

Anal. Calcd. for $C_{10}H_{10}F_4O$: C, 54.05; H, 4.55; F, 34.20. Found: C, 55.02, 54.92; H, 4.90, 4.84; F, 33.26, 33.38.

2-Acetoxymethylbicyclo[2.2.1]-2,5-heptadiene (VI). A mixture of 25 g. (0.205 mole) of V, 50 ml. of benzene and 50 ml. of pyridine was cooled to 0°. A solution of 17 g. of acetyl chloride (0.218 mole) dissolved in 50 ml. of benzene was added dropwise while maintaining reaction temperature between 40–50°. After complete addition of the acetyl chloride, the reaction mixture was maintained at 50° for 1 hr., cooled to room temperature and diluted with 150 ml. of ether and 150 ml. of water. The organic phase was washed successively with two 100-ml. portions of 3*N* hydrochloric acid solution, two 50-ml. portions of water, and two 50-ml. portions of 20% sodium hydroxide solution. The organic phase was dried with magnesium sulfate, filtered, and the solvent was removed. The residue was distilled to give 22.7 g. (67% yield) of product, b.p. 80–82°/4 mm., n_D^{25} 1.4744.

Anal. Calcd. Ester equiv. 164.2. Found: 165 and 167.

Preparation of VIII. Ethyl propiolate (19 g., 0.19 mole) was heated with 47 g. (0.17 mole) of hexachlorocyclopentadiene for 15 hr. at 140–145° and allowed to stand overnight at room temperature. The product was distilled to give 48.3 g. of product, b.p. 122–129°/0.5–0.6 mm., n_D^{25} 1.5394. The product crystallized on standing having m.p. 45–48°.

Anal. Calcd. for $C_{10}H_6Cl_6O_2$: C, 32.35; H, 1.63; Cl, 57.36. Found: C, 32.81, 32.70; H, 1.88, 1.93; Cl, 57.61.

2-Trifluoromethylbicyclo[2.2.1]-2,5-heptadiene (IX). Trifluoromethylacetylene has been reported.[17,18] It was prepared in our case by R. J. Harder of the Central Research Department of E. I. du Pont de Nemours and Co., by a reported procedure.[19] Seventeen grams of trifluoromethylacetylene, 25 g. of diethyl ether, 14 g. of cyclopentadiene and 0.1 g. hydroquinone were heated in an autoclave at 50° for 12 hr. The ether was removed and the product distilled at 52°/100 mm.

Anal. Calcd. for $C_8H_7F_3$: C, 60.00; H, 4.41; F, 35.59. Found: C, 60.41, 60.50; H, 4.44, 4.72; F, 35.74, 35.88.

Attempted polymerization of VIII *with a coordination catalyst.* Ten grams of VIII was dissolved in 10 ml. of benzene to which was added 0.3 ml. of aluminum isobutyl (0.03 mmole) and 0.06 ml. of vanadium oxytrichloride–titanium tetrachloride (1:1) (0.06 mmole). The resulting solution was stirred at room temperature for 24 hr. without any observable viscosity change. No polymer precipitated when the solution was added to 100 ml. of methanol.

Attempted polymerization of IX. Six grams of IX was heated with 0.06 g. of azodiisobutyronitrile for 48 hr. at 60°. No viscosity increase was observed. IX was isolated from the reaction mixture by distillation as described above giving 3.3 g. of IX. This 3.3-g. sample of IX was treated with 0.033 g. of azodiisobutyronitrile at 60° for 48 hr. after which time the reaction mixture was added to 100 ml. of methanol giving less than 0.1 g. of a white precipitate. This precipitate melted with decomposition at 250–260°, was soluble in acetone, and analyzed to give 32.07 and 32.29% fluorine. This may be a low yield of polymer.

Attempted polymerization of X *and* XI. The preparation will be reported. A 1-g. sample of X was heated at 60° with 0.01 g. azodiisobutyronitrile for 16 hr. No change in viscosity of the material occurred. The index of refraction of starting material was n_D^{25} 1.4768 and of treated material n_D^{25} 1.4760.

A 1-g. sample of XI was treated as described for X. No viscosity change was observed. The index of refraction of starting material was n_D^{25} 1.4667 and of treated material n_D^{25} 1.4675.

PHILADELPHIA, PA.

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