Sodium 1H,1H,ωH-fluoroalocoholates. Sodium wire dissolved readily in three to fourfold molar excess of 1*H*,1*H*,3*H*-tetrafluoropropanol or 1*H*,1*H*,5*H*-octafluoropentanol at 80–90° with formation of the alcoholates. When equivalent amounts of 1*H*,1*H*,5*H*-octafluoropentanol and sodium were treated in ether or in dioxane at the reflux for long periods, the metal was not completely consumed. A brown film of carbonaceous material formed on the sodium particles and finally brought the reaction to a stop.

Sodium fluoroalcoholates are best prepared by the reaction of equimolar amounts of fluoro alcohol and sodium hydride in ether, and can be precipitated from ether solutions with dry xylene. The compounds should not be heated in the absence of solvents as violent decompositions may occur.[16]

Potassium 1H,1H,ωH-fluoroalcoholates. The formation of potassium fluoroalcoholates was carried out in dimethoxytetraethylene glycol at 84°. Small pieces of the metal were added to the stirred mixture under anhydrous conditions in a nitrogen atmosphere. Use of potassium in this reaction is much more dangerous than sodium, explosions having occurred even in the absence of air.

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(16) E. J. P. Fear, J. Thrower, and J. Veitch, *J. Chem. Soc.*, 1323 (1958).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF IOWA]

Polymerization by the Diels-Alder Reaction[1,2]

J. K. STILLE AND L. PLUMMER

Received April 10, 1961

Polymerization reactions which utilize the Diels-Alder reaction as a propagation mechanism to produce high molecular weight polymers have been successfully accomplished. Three biscyclopentadienes, 1,6-bis(cyclopentadienyl)hexane, 1,9-bis(cyclopentadienyl)nonane and α,α'-bis(cyclopentadienyl)-*p*-xylene have been prepared. These monomers have been homopolymerized and copolymerized with the didienophiles *p*-benzoquinone and *N,N'*-hexamethylenebismaleimide. The results of the polymerization studies and the studies of polymer structure demonstrate that the homopolymerizations take place by a Diels-Alder reaction in which the monomer acts both as a diene and a dienophile while in the copolymerization reactions the biscyclopentadiene compounds serve as didienes.

A polymerization which utilizes a Diels-Alder reaction for propagation to yield high molecular weight polymers has only recently been investigated.[3-6] Cyclopentadiene readily dimerizes at room temperature, and at elevated temperatures over longer periods of time, a trimer, tetramer, pentamer, hexamer and other higher molecular weight polymers are formed.[7] Although a portion of the higher molecular weight polymer is a result of vinyl addition polymerization, the oligomers are formed through successive additions of cyclopentadiene through a Diels-Alder reaction.[8]

The fact that cyclopentadiene and methylcyclopentadiene readily dimerize by serving both as a diene and a dienophile in a Diels-Alder reaction and the fact that these dienes readily react with a wide variety of dienophiles, prompted the investigation of a series of biscyclopentadienyl compounds. Such a compound should be able to undergo not only a homopolymerization reaction but also a copolymerization reaction with a didienophile.

Substituted ferrocene derivatives have been prepared from biscyclopentadienylalkanes which were not isolated as such but used *in situ*.[9] The polymerization of α,α'-bis(cyclopentadienyl)-*p*-xylene has been reported to give an insoluble polymer by a Diels-Alder propagation,[10] but this polymer is probably the result of extensive vinyl addition polymerization.

The preparation of 1,6-bis(cyclopentadienyl)hexane (Ia), 1,9-bis(cyclopentadienyl)nonane (Ib) and α,α'-bis(cyclopentadienyl)-*p*-xylene (Ic) was carried out by the addition of cyclopentadienyl sodium to the appropriate dibromide. The products could not be suitably purified by crystallization and attempted distillation led to rapid polymerization of these monomers. The liquid monomers were partially purified by repeated slow precipitations

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(2) Presented in part at the September 1959 Meeting of the American Chemical Society, Atlantic City, N. J.

(3) W. J. Bailey and J. Economy, Abstracts of Papers Presented at the 126th Meeting of the American Chemical Society, New York, N. Y., September 12–17 (1954) p. 195.

(4) W. J. Bailey, J. Economy, and M. E. Hermes, Preprints of Papers Presented at the Division of Polymer Chemistry, 138th Meeting of the American Chemical Society, New York, N. Y., September 12–16 (1960) p. 1.

(5) E. A. Kraimen, U. S. Patent **2,890,206** and **2,890,207**, June 9, 1959.

(6) J. S. Meek, P. A. Argabright, and R. D. Stacy, Abstracts of Papers Presented at the 134th Meeting of the American Chemical Society, Chicago, Ill., September 7–12 (1958) p. 23p.

(7)(a) H. Staudinger, *Ann.*, **467**, 73 (1928). (b) H. Staudinger and H. Bruson, *Ann.*, **447**, 97 (1926).

(8) (a) K. Alder and G. Stein, *Ann.*, **485**, 223 (1931). (b) K. Alder and G. Stein, *Ann.*, **496**, 204 (1932). (c) K. Alder and G. Stein, *Ber.*, **67**, 613 (1934).

(9) A. Luttringhaus and W. Kullick, *Angew. Chem.*, **70**, 438 (1958).

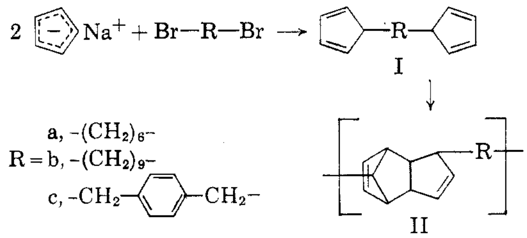
(10) R. W. Upsom, U. S. Patent **2,776,232**, Dec. 6, 1955.

TABLE I

BISCYCLOPENTADIENE POLYMERS

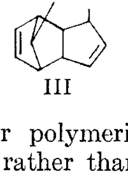
Polymer	Polymerization Solvent	Time, Hr.	Temperature, °	% Conversion	η^a	Softening Temperature
IIa	Toluene	24	Reflux	90	0.042	Viscous oil
IIb	Benzene	24	Reflux	75	—	Viscous oil
IIc	Benzene	24	Reflux	74	0.12	160d
IIc	Benzene	72	25	70	0.084	160d
IVa	Benzene	16	Reflux	74	0.10	125
IVa	Benzene	24	Reflux	88	0.13	125
IVa	Toluene	24	Reflux	62	0.065	125
IVa	Xylene	24	Reflux	Low	—	—
IVa	Benzene	168	25	73	0.12	125
IVb	Benzene	24	Reflux	75	0.13	110
IVb	Benzene	72	25	70	0.13	110
IVc	Benzene	24	Reflux	73	0.091	180
IVc	Benzene	72	25	62	0.11	180
Va	Benzene	24	Reflux	97	0.10	140
Vb	Benzene	24	Reflux	78	0.18	120
Vc	Dimethylformamide	24	Reflux	82	0.22	240

[a] Inherent viscosities were obtained from solutions of 0.25 g. of polymer/100 ml. of benzene.



at −78°, and were obtained as waxy solids at this temperature. The inability to obtain crystalline monomeric products may be due to several factors. The analyses of Ia–c indicated contamination with minor amounts of cyclopentadienyl compounds in which substitution had taken place at only one end of the dibromide. In addition the infrared spectra showed maxima characteristic of both cyclopentadiene and dicyclopentadiene, thus indicating some polymerization to dimer, trimer, etc. had taken place.

Since molecular models indicated that 1,9-bis-(cyclopentadienyl)nonane would be capable of an intramolecular Diels-Alder reaction to form the adduct III, an attempt was made to prepare this adduct in order to obtain a pure crystalline monomer which could be either homopolymerized by a ring-opening reaction or copolymerized with various didienophiles. The attempt was unsuccessful, since intermolecular polymerization occurred at room temperature, rather than the desired intramolecular reaction, even though a dilute solution was used.



III

It is unlikely that these monomers are mixtures of isomers which differ by the position of attachment of the R group on the cyclopentadienyl portion, since the cyclopentadienylsodium was added in the presence of excess dibromide by slow inverse addition.

Bulk polymerization of Ia–c even in the presence of free radical inhibitors gave insoluble thermosetting polymers, undoubtedly through a vinyl-type addition polymerization. Homopolymerization of Ia and Ib in solution afforded low molecular weight oils while homopolymerization of Ic produced a solid high molecular weight polymer which was soluble in various organic solvents and had an inherent viscosity of 0.12 (Table I). The infrared spectra of these homopolymers exhibited maxima characteristic of dicyclopentadiene. The polymers readily crosslinked on exposure to the atmosphere.

The didienophiles chosen for copolymerization reactions with Ia–c were *p*-benzoquinone and *N,N'* - hexamethylenebismaleimide. Quinone is known to undergo a Diels-Alder reaction with two moles of cyclopentadiene to form the adduct 1,4,4a,5,8,8a,9a,10a - octahydro - 1,4,5,8 - dimethano-9,10-anthraquinone.[11,12] The reaction of *N,N'*-hexamethylenebismaleimide with two moles of cyclopentadiene was found to give a suitable yield of *N,N'* - hexamethylenebis(3,6 - endomethylene-Δ^4-tetrahydrophthalimide).

The copolymerization reactions of Ia–c with *p*-benzoquinone or *N,N'*-hexamethylenebismaleimide in solution yielded high molecular weight 1:1 copolymers. (Table 1). The structures of these copolymers were assigned on the basis of elemental analyses and the comparison of their infrared spectra with the spectra of the model compounds 1,4,4a,5,8,8a,9a,10a-octahydro-1,4,5,8-dimethano - 9,10 - anthroquinone and *N,N'*-hexamethylenebis(3,6 - endomethylene - Δ^4 - tetrahydrophthalimide). All the copolymers exhibited bands near 700 cm.$^{-1}$, characteristic of the nor-

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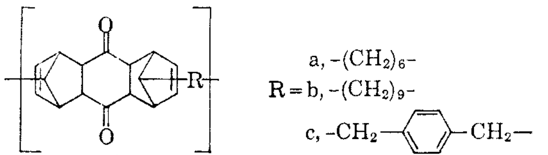
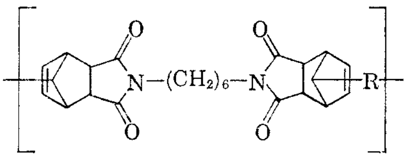
(11) W. Albrecht, *Ann.*, **348,** 31 (1906).

(12) K. Alder and G. Stein, *Ann.*, **501,** 247 (1933).



IV



V

bornene moiety.[13] The copolymers are completely soluble in benzene, have softening points in the range 110–240°, and inherent viscosities as high as 0.22 have been obtained with certain samples.

Although the infrared data support the fact that the didiene monomers (Ia–c) are actually mixtures of monomer, dimer, trimer, etc., this does not exclude the fact that 1:1 copolymers can be formed. Dicyclopentadiene itself readily reacts with active dienophiles by first undergoing a reverse Diels-Alder reaction.

By contrast, a hard brittle insoluble copolymer has been claimed as a result of the bulk polymerization of Ic with *N,N'*-(1,3-phenylene)bismaleimide.[10] This polymer was evidently not formed through a Diels-Alder reaction but by a vinyl addition polymerization since the polymer was insoluble and the ratio of maleimide portions to biscyclopentadienyl portions was 15.6:1.

In the determination of the optimum temperatures for the copolymerization of Ia with *p*-benzoquinone, the reaction was carried out in refluxing benzene, toluene, and xylene. Since the inherent viscosity of the resulting copolymer decreased as the reflux temperature of the solvent increased, it is apparent that the reverse Diels-Alder reaction becomes important at elevated temperatures.

The observations that (1) the polymers formed in these polymerization reactions are completely soluble in organic solvents, (2) the infrared spectra of the polymers exhibit the same characteristic maxima as observed in certain model Diels-Alder compounds, and (3) the monomers Ia–c form exactly 1:1 copolymers with both *p*-benzoquinone and *N,N'* - hexamethylenebismaleimide, demonstrate that these polymerization reactions utilize the Diels-Alder synthesis as a propagation reaction to produce high molecular polymers.

EXPERIMENTAL

1,6-Bis(cyclopentadienyl)hexane (Ia). A solution of cyclopentadienylsodium in 200 ml. of tetrahydrofuran was prepared from 11.5 g. (0.5 g.-atom) of sodium and 33.05 g. (0.5 mole) of freshly cracked cyclopentadiene.[14] This solution at 0° was added dropwise over a period of 1 hr. to a rapidly stirred solution of 61 g. (0.25 mole) of 1,6-dibromohexane in 300 ml. of tetrahydrofuran which had previously been cooled to 0°. Stirring was continued for an additional hour at 0° after which time the reaction mixture was decomposed by 125 ml. of a saturated solution of ammonium chloride at −10°. The organic layer was removed, the aqueous layer was extracted with three 100-ml. portions of cold ether and the combined organic layer was dried over magnesium sulfate at −5° for 16 hr. in the presence of 0.1 g. of *N*-phenyl-β-naphthylamine inhibitor. The volume of the organic solution was reduced to 300 ml. at 0° under reduced pressure, methanol was added and the solution was slowly cooled to −78°. The white waxy precipitate obtained was removed and successive concentrations and precipitations gave additional product. The precipitate contained a greater portion of solid tetrahydrofuran and 1,6-bis(cyclopentadienyl)hexane. The tetrahydrofuran was removed at 0° under reduced pressure to give 39.5 g. (74%) of crude product. The product was an oil at 0° which was purified by reprecipitation from an ether-methanol solution at −78°. The product could not be purified by distillation as rapid polymerization occurred.

Anal. Calcd. for $C_{16}H_{22}$: C, 89.66; H, 10.34. Found: C, 89.06; H, 9.98.[15]

The infrared spectrum showed absorption maxima at 3070 (=CH str.), 2900 and 2850 (—C—H str.), 1620 (C=C str.) and 895 cm.$^{-1}$ (=CH wag) characteristic of the monomer and a weak maximum at 724 cm.$^{-1}$, a characteristic of the norbornene moiety found in dicyclopentadiene.

1,9-Bis(cyclopentadienyl)nonane (Ib). The preparation of 1,9-bis(cyclopentadienyl)nonane from 32.4 g. (0.49 mole) of cyclopentadiene, 11.3 g. (0.49 g.-atom) of sodium and 70 g. (0.24 mole) of 1,9-dibromononane in a tetrahydrofuran solvent was carried out as described for Ia.

In an attempt to cyclize Ib by an intramolecular Diels-Alder reaction, the organic solution containing Ib was divided into two equal portions. The first portion was diluted to 800 ml. with tetrahydrofuran and stirred at room temperature for 3 days under a nitrogen atmosphere. Only polymeric material was isolated.

The second portion was treated as described for Ia to obtain 20.2 g. (65%) of 1,9-bis(cyclopentadienyl)nonane.

Anal. Calcd. for $C_{19}H_{28}$: C, 89.00; H, 11.00. Found: C, 88.35; H, 10.00.

The infrared spectrum showed maxima at 3050 (=CH str.), 2880 and 2830 (—CH str.), 1613 (C=C str.), 895 (=CH wag), and 722 cm.$^{-1}$ (=CH wag).

α,α'-Bis(cyclopentadienyl)-p-xylene (Ic). The preparation of Ic from 21.16 g. (0.30 mole) of cyclopentadiene, 6.95 g. (0.30 g.-atom) of sodium (200 ml. of tetrahydrofuran) and 39.6 g. (0.15 mole) of α,α'-dibromo-*p*-xylene in 1 l. of tetrahydrofuran was carried out as described for the preparation of Ia. The volume of the organic solution containing Ic was reduced to 400 ml. for the precipitation to yield 19.5 g. (55.5%) of Ic. This monomer polymerized too rapidly for an analysis on mostly monomeric material. Analysis was obtained on the polymer, however (Table II). A freshly prepared sample which had been kept at −78° until just prior to taking the infrared spectrum showed maxima at 3130 (=CH str.), 2890 and 2860 (—CH str.), 1604 (C=C str.), 950 and 889 cm.$^{-1}$, characteristic of the monomer and strong maxima at 752 and 723 cm.$^{-1}$, which are found in dicyclopentadiene.

N,N'-Hexamethylene bismaleimide. This didienophile was prepared as described[16] except that the following modifications were imposed.

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(13) S. J. Cristol and R. L. Snell, *J. Am. Chem. Soc.*, **80,** 1950 (1958).

(14) G. Wilkinson, *Org. Syntheses*, **36,** 31 (1956).

(15) Analyses were performed by Mr. Don Ries and Mr. R. T. Foster, University of Iowa, Iowa City, Iowa, and Micro-Tech Laboratories, Skokie, Ill. The infrared spectra were run on a Perkin-Elmer Model 21 infrared spectrophotometer.

(16) N. E. Searle, U. S. Patent **2,444,536,** July 6, 1948.

TABLE II

ANALYTICAL DATA FOR POLYMERS

Polymer	Formula	Calcd.			Found			Infrared Maxima, cm.$^{-1}$
		C	H	N	C	H	N	
IIc	$(C_{18}H_{18})_n$	92.38	7.62	—	89.20	7.52	—	765, 725, 672[a]
IVa	$(C_{22}H_{26}O_2)_n$	81.95	8.07	—	82.09	8.33	—	1695, 905, 732[b]
IVb	$(C_{25}H_{32}O_2)_n$	82.63	8.86	—	81.01	8.81	—	1694, 903, 730[b]
IVc	$(C_{24}H_{22}O_2)_n$	84.20	6.48	—	83.80	6.55	—	1678, 916, 730[b]
Va	$(C_{30}H_{38}N_2O_4)_n$	73.44	7.81	5.71	—	—	5.76	1770, 1695, 722[c]
Vb	$(C_{33}H_{44}N_2O_4)_n$	74.40	8.33	5.50	73.40	8.44	5.95	1770, 1702, 724[c]
Vc	$(C_{32}H_{34}N_2O_4)_n$	75.27	6.12	5.48	74.84	6.44	5.02	1765, 1700, 724[c]

[a] Present in the spectrum of dicyclopentadiene. [b] The infrared spectrum of 1,4,4a,5,8,8a,9a,10a-octahydro-1,4,5,8-dimethano-9,10-anthraquinone,[11,12] shows maxima at 1693 (C=O str.), 912 and 729 cm.$^{-1}$ (=CH wag norbornene). [c] Compare to the infrared spectrum of *N,N'*-hexamethylenebis(3,6-endomethylene-Δ^4-tetrahydrophthalimide).

A 50:1 molar ratio of acetic anhydride solvent to *N,N'*-hexamethylenebismaleamic acid and a quantity of sodium acetate which corresponded to 10% of the molar amount of acetic anhydride, was employed in the conversion of *N,N'*-hexamethylenebismaleamic acid to *N,N'*-hexamethylenebismaleimide. From 25 g. (0.08 mole) of the maleamic acid was obtained 6.7 g. (30%) of the bismaleimide after two recrystallizations, m.p. 140–141°, reported[16] 139–140°.

N,N'-Hexamethylenebis(3,6-endomethylene-Δ^4-tetrahydrophthalimide). A solution of 1 g. (0.0036 mole) of *N,N'*-hexamethylenebismaleimide in 35 ml. of tetrahydrofuran was added to 0.52 g. (0.0079 mole) of freshly cracked cyclopentadiene. The mixture was allowed to remain at 25° for 24 hr., after which time the solvent was removed under reduced pressure leaving a solid residue. The residue was recrystallized twice from a methanol-water mixture to yield 0.50 g. (40%) of white needles, m.p. 133–134°.

Anal. Calcd. for $C_{24}H_{28}O_4N_2$: C, 70.57; H, 6.90; N, 6.85. Found: C, 70.07; 6.84; N, 6.79.

The infrared spectrum showed maxima at 3050 (=CH str.), 2940 and 2855 (—CH str.), 1765 and 1695 (imide C=O str.), 842 and 720 cm.$^{-1}$ (=CH wag).

Homopolymerization of Ia–c. In all homopolymerization reactions, *N*-phenyl-β-naphthylamine was added as a free radical inhibitor. Polymerizations in bulk carried out at temperatures from 10° to 140° afforded only insoluble rubbery to hard thermosetting polymers.

Solution polymerizations of Ia and Ib which were carried out in refluxing aromatic solvents gave only low molecular weight oils IIa, IIb (Table I) which were soluble in benzene, carbon tetrachloride and carbon disulfide. The infrared spectra of these polymers showed maxima at 724 cm.$^{-1}$.

Solution polymerizations of Ic carried out in benzene gave a solid polymer IIc (Table I) which was purified by reprecipitation from benzene by methanol. Exposure of the polymer to air for a few hours produced an insoluble polymer. Analytical data on IIc are shown in Table II.

Copolymerization of Ia–c. The results of the copolymers of Ia–c with *p*-benzoquinone and *N,N'*-hexamethylenebismaleimide are shown in Table I. The analyses of these polymers are given in Table II. In each case 0.01 mole of *p*-benzoquinone or *N,N'*-hexamethylenebismaleimide was dissolved in 25 ml. of solvent. To this solution was added a solution of 0.01 mole of Ia, Ib, or Ic in 25 ml. of solvent. In the case of polymers Va–c, a small amount of *N*-phenyl-β-naphthylamine was added as a free radical inhibitor. The polymers were precipitated twice from benzene by methanol or pentane and subjected to freeze drying from a benzene solution.

IOWA CITY, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

Reaction Rates by Distillation. IX. The Condensation of Anilines with Benzaldehydes

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The acid-catalyzed condensation of aniline with benzaldehyde in benzene containing tributylamine as a "leveller" has been found to be first order with respect to each reactant and the catalyst. Electron-releasing *para* substituents decrease the rate when on the benzaldehyde and increase the rate when on the aniline; a satisfactory "rho-sigma" correlation is obtained in each case. The results are consistent with a mechanism closely analogous to those favored for related reactions.

The reaction of anilines with benzaldehydes has been studied by the distillation method[2] because of the significance of the reaction itself as well as the potential value of the results in elucidating the course of the related condensation of anilines with benzoins.[3]

$$p\text{-}RC_6H_4CHO + p\text{-}R'C_6H_4NH_2 \longrightarrow p\text{-}RC_6H_4CHOHNHC_6H_4R'\text{-}p \tag{1}$$

$$p\text{-}RC_6H_4CHOHNHC_6H_4R'\text{-}p \longrightarrow p\text{-}RC_6H_4CH{=}NC_6H_4R'\text{-}p + H_2O \tag{2}$$

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(1) From a portion of the Ph.D. thesis of M. J. Kamlet, March, 1954.

(2) For the preceding paper in this series see E. F. Pratt and H. J. E. Segrave, *J. Am. Chem. Soc.*, 81, 5369 (1959).

(3) E. F. Pratt and M. J. Kamlet, to be published.