TABLE II

HOFMANN ELIMINATION OF N,N,N-TRIMETHYL-2-t-BUTYL-3,3-DI-METHYLBUTYLAMMONIUM HYDROXIDE-2-d_1

Compound	Millimoles
Quaternary iodide used	1.94
Quaternary iodide recovd.	0.35
Trimethylamine formed, total	.875
1,1-Di-t-butylethylene formed, total	.686
Dimethyl ether formed,[a] total	.039
Tertiary amine 7 formed,[b] total	.235

[a] Presumably arising by displacement of a methyl group from the quaternary nitrogen by methoxide (in equilibrium with methanol formed by a prior displacement). [b] By displacement.

To the unchanged hydroxide (pot residue) were added 3 ml. of water and 3 ml. of ether, and the aqueous layer was acidified by dropwise addition of hydriodic acid. The solution was evaporated to dryness under reduced pressure and the residue was washed with cold acetone, leaving the methiodide as a white crystalline solid.

N,N-Dimethyl-2,2-di-t-butylethylamine-2-d_1 (7) from the Methiodide 10.—Samples of the starting methiodide and of the above methiodide from the quaternary hydroxide were separately reduced with lithium aluminum hydride in refluxing tetrahydrofuran for 96–144 hr.[22] Water and 30% aqueous sodium hydroxide were added, the solutions were filtered and the precipitates were washed several times with ether. The solvents were distilled and samples of the amine were collected by gas chromatography for analysis by mass spectrometry. The mass spectra of the two samples showed the deuterium distribution

	d_0, %	d_1, %	d_2, %
Amine 7, before Hofmann	6.5	93.4	0.1
Amine 7, after Hofmann	5.7	92.2	2.0

The difference in analyses indicates the amount of exchange occurring during the Hofmann elimination; deuterium analysis[18] of 7, before Hofmann: 0.923 atom of deuterium per molecule.

Methyl-d_1 p-Toluenesulfonate (11).—Formaldehyde, obtained by heating paraformaldehyde at 130–150°, was passed under nitrogen through an electrically heated tube into a stirred solution of a slight excess of lithium aluminum deuteride in ether. The excess deuteride was decomposed with the requisite amount of water, and one equivalent of p-toluenesulfonyl chloride (based

on formaldehyde) was added, followed by one equivalent of 30% sodium hydroxide solution with vigorous stirring over a 2-hr. period. The temperature was kept below 28° during the addition. The mixture was acidified with 5% hydrochloric acid and extracted with ether, and the combined extracts were washed with saturated sodium bicarbonate solution and water, and dried over magnesium sulfate. The ether was removed under reduced pressure and the residue was chromatographed on silica gel. Unchanged tosyl chloride was eluted with benzene and the desired methyl-d_1 p-toluenesulfonate with ether. The tosylate was distilled, b.p. 154° (7 mm.); the maximum yield obtained was about 25%; deuterium analysis[20]: d_0, 4.94%; d_1, 94.8%; d_2, 0.22%. When a large excess of formaldehyde was used the deuterium content was: d_0, 9.8%; d_1, 90.2%; d_2, 0%.

Trimethylamine-d_1.—A mixture of 3.03 g. of methyl-d_1 p-toluenesulfonate, 9 ml. of anhydrous dimethylamine and 17 ml. of dry benzene was heated at 100° in a sealed tube for 12 hr. The tube was cooled to −70°, 15 ml. of concentrated hydrochloric acid was added and the mixture was warmed to room temperature and then evaporated to dryness. To the cooled residue (13.5 g.) dissolved in 50 ml. of water was added a cold solution of sodium hydroxide (17.2 g.) in water (50 ml.) followed by 20 ml. of benzenesulfonyl chloride. The mixture was shaken at room temperature for 4 hr., cooled and acidified with concentrated hydrochloric acid. N,N-Dimethylbenzenesulfonamide and excess benzenesulfonyl chloride were extracted from the mixture with ether. The aqueous layer was evaporated to dryness and the trimethylamine-d_1 hydrochloride was extracted from the residue with chloroform using a Soxhlet extractor. After removal of the chloroform the residual semisolid was treated with 50% sodium hydroxide solution and the liberated trimethylamine-d_1 gas was dissolved in concentrated hydrochloric acid. The basic solution was heated to drive out all of the dissolved trimethylamine. The aqueous acidic solution was evaporated to dryness and the residue was recrystallized from absolute ethanol; m.p. 281.8–282.2° dec.

Trimethylamine-d_1, obtained by the addition of aqueous base to the pure hydrochloride, was collected by distillation at 3 mm. in a trap cooled by liquid nitrogen.

Trimethylamine-d_1 picrate (90% yield, m.p. 218°) was prepared and had m.p. 223° after 3 recrystallizations from absolute ethanol.

Anal. Calcd. for $C_9H_{11}DN_4O_7$: C, 37.38; H + D, 4.18; N, 19.37. Found: C, 37.28; H + D, 4.31; N, 19.06; deuterium analysis[18]: 0.954 atom per molecule.

(22) The procedure is described by A. C. Cope, E. Ciganek, L. J. Fleckenstein and M. A. P. Meisinger, *J. Am. Chem. Soc.*, **82**, 4651 (1960).

Polycondensation of Ferrocenylcarbinols and Substitution Orientation Effects[1]

BY EBERHARD W. NEUSE AND DANIEL S. TRIFAN

Based on previous studies on the reaction of ferrocene with representative α-arylcarbinols, self-condensation reactions of three ferrocenylcarbinols, hydroxymethylferrocene, (1-hydroxyethyl)-ferrocene and α-hydroxybenzylferrocene, resulting in the formation of −CH(R)− linked ferrocenylene polymers are described. The acid-catalyzed reactions are conducted in the melt phase and lead to crude reaction products in the M_n range 1000–6000. The polymers are soluble in a number of organic solvents, and the lower members show a defined melting range. Quantitative infrared spectroscopic analysis has been applied to elucidate structural correlations and the effect of variables on the ring substitution orientations occurring under these conditions of polymer formation compared to the general behavior of the ferrocene nucleus under usual non-polymeric conditions.

Introduction

As part of a comprehensive study of carbinol condensations with the ferrocene nucleus, a previous investigation[2] has dealt with the condensation of ferrocene with representative α-arylcarbinols in the melt phase, rapid, almost quantitative reaction being exhibited by the limiting case of triphenylcarbinol, decreasing to slow, very slight conversions with primary α-arylsubstituted alcohols. In the present work, we have investigated the characteristics of the self-condensation reactions of some ferrocenylcarbinols, utilizing both

the highly nucleophilic character of the ferrocene ring as well as the high rate of ionization of metallocenyl α-carbinyl derivatives,[3] whose origin has been established as a general metal–electron backside participation with resulting metallocarbonium cation structures of the type I.[4] Under conditions as earlier applied,[2] a rapid self-condensation of ferrocenylcarbinols was thus anticipated, in its final stage leading to polymeric compounds consisting of ferrocenylene and methylene or methine groups alternating along the

(1) This research was supported by the Army, Navy and Air Force under Signal Corps Contract DA-039sc-78105.

(2) E. W. Neuse and D. S. Trifan, *J. Am. Chem. Soc.*, **84**, 1850 (1962).

(3) (a) N. Weliky and E. S. Gould, *ibid.*, **79**, 2742 (1957); (b) J. H. Richards and E. Hill, *ibid.*, **81**, 3484 (1959).

(4) (a) D. S. Trifan and R. Bacskai, *Tetrahedron Letters*, No. 13, 1 (1960); (b) E. Hill and J. H. Richards, *J. Am. Chem. Soc.*, **83**, 4216 (1961).

chain. A comparison of the substitution orientation effects involving polymeric reactants with those in some previously elucidated monomer cases were also of especial interest here.

Results and Discussion

Three representative ferrocenylcarbinols, IIa, IIb and IIc, were investigated in the present study. The results have shown that under proper conditions favoring cation formation and subsequent electrophilic

I

IIa, R = H
 b, R = CH₃
 c, R = C₆H₅
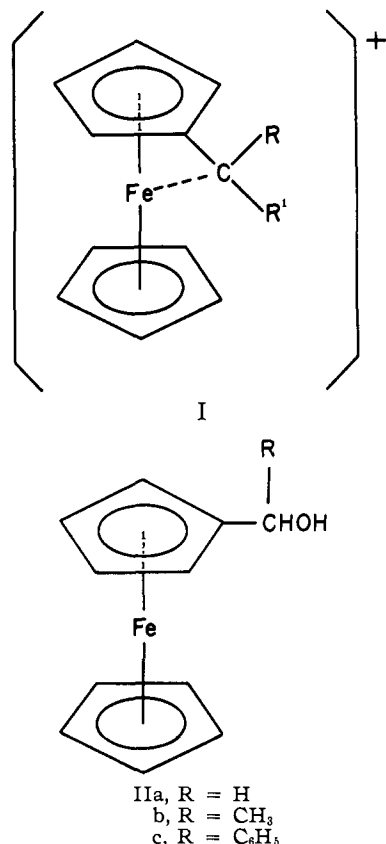
attack on the ferrocene ring, polymers of the expected composition $+C_{10}H_8Fe-CHR+$ are readily formed, with yields up to 96%. There is a marked contrast between this reaction course taken by ferrocenylcarbinols in the present work and that taken in concentrated sulfuric and hydrofluoric acid media where only formation of dinuclear, non-polymeric products has been observed.[5] Under such conditions, cation coupling leading to 1,2-diferrocenylethanes has been demonstrated by Rinehart, et al.,[5d] for both hydroxymethylferrocene and its precursors, ferrocene–formalin (in H_2SO_4),[5b] and ferrocene–paraformaldehyde (in HF, 100°),[5a] as well as for ferrocene–benzaldehyde,[5a,b] while Pauson has succeeded in obtaining diferrocenylmethane by effecting cation condensation on the ferrocene nucleus under somewhat similar conditions[5e] in concentrated sulfuric acid through use of ferrocene–paraformaldehyde and ferrocene–hydroxymethylferrocene mixtures. The dependence of the instantaneous concentrations of cations and ferrocene nuclei on the variations in reaction conditions appears to determine importantly which of these alternative mechanisms prevails. Some indication of the possibility of a small extent of cation coupling occurring in the present work in the case of hydroxy-

(5) (a) V. Weinmayr, J. Am. Chem. Soc., 77, 3009 (1955); (b) A. N. Nesmeyanov and I. I. Kritskaya, Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk, 253 (1956); (c) R. Riemschneider and D. Helm, Ber., 89, 155 (1956); (d) K. L. Rinehart, Jr., C. J. Michejda and P. A. Kittle, J. Am. Chem. Soc., 81, 3162 (1959); (e) P. L. Pauson and W. E. Watts, J. Chem. Soc., 3880 (1962).

methylferrocene (IIa) is noted later (footnote 29); otherwise under the present bulk concentration conditions at low catalyst concentrations employed here, the reactions proceeded cleanly via nuclear substitution to give only polymeric products.

The carbinols were heated above their melting points under nitrogen for various periods of time in the presence of 0.5–2% acidic catalysts.[6] While a few experiments were conducted with hydrochloric acid for comparison, preference was given to compounds of the Lewis acid type, $ZnCl_2$ being particularly convenient for these readily ionized ferrocenyl derivatives. Polycondensation proceeded via the corresponding dinuclear ethers, as was demonstrated in experiments starting with carbinols IIa and IIb, from which the ethers could be intercepted almost quantitatively during the initial phase of the reaction. Accordingly, the final course of polycondensation was the same when the di-(ferrocenylcarbinyl) ethers were directly employed as the starting materials. As heating was continued and the eliminated water driven off, the melt equilibrium shifted at the expense of these intermediates toward the formation of higher-molecular components, in which, eventually, ether linkages could no longer be detected. Under standard conditions using Lewis acids, the dinuclear ethers essentially vanished from the mixture within less than 1 hr.

Depending on the reaction conditions, number-average molecular weights, M_n, were found ranging from ca. 1000 to 6000.[7] Mineral acids as catalysts led to polymers with M_n values not exceeding 3000.[7] With Lewis acids an increase in M_n was noticeable; the highest values were attained by employing $AlCl_3$. Generally, after a certain reaction period, the molecular weight reached a maximum value at a given temperature and catalyst type and concentration, and excessive heating eventually resulted in partial decomposition. Therefore, reaction times and temperatures were maintained at a minimum level necessary to ensure optimum conversion.

For the final condensation products, quantitative elemental analyses, coupled with molecular weight determinations performed on carefully fractionated polymer, were in agreement with the novolac-type structures III. This can be seen from Table I, in which elemental composition data are summarized for five typical fractions of polymer from hydroxymethylferrocene (IIa), each fraction representative of a certain molecular weight range, together with corresponding data for the polymer series derived from (1-hydroxyethyl)-ferrocene (IIb) and α-hydroxybenzylferrocene (IIc).

In agreement with the polymer structures III, infrared spectra of the fractionated polycondensation products exhibited the well known absorption bands typical of the substituted ferrocene system[8] as well as those due to the various known vibrational modes of

(6) Throughout this paper, all catalyst concentrations are given in per cent by weight of starting material.

(7) Determined on unfractionated material of relatively broad molecular weight distribution.

(8) Some less known bands were previously reported (ref. 2). In the 7.10–7.20 μ range, the band at 7.08 μ, distinctly exhibited by lower members, loses in intensity with increasing M_n as does a second weak band in this region near 7.20 μ. With polymers IIIa as with monomeric model compounds containing the $C_{10}H_9Fe \cdot CH_2-$ residue, the 8.15-μ peak was found to be shifted toward lower frequencies (8.18–8.20 μ). The band at 9.65 μ, while of medium intensity in IIIb, was strong in IIIa and IIIc. In the latter class, due to overlap by absorption owing to ν_{18a} of the monosubstituted benzene ring, it formed a broad doublet with the 9.80 μ band. In IIIa, it showed enhanced intensity with rising M_n. In all polymers, the C–H bending absorption in the 12.20–12.30 μ region, usually of sharp contours in monomeric compounds, was considerably broadened as the molecular weight increased. The two bands near 11.70 and 11.90 μ were visible as shoulders only (frequently hidden), as were those near 12.80 and 13.10 μ.

TABLE I

No.[a]	Poly-mer series	M.p.,[b] °C.	M_n	C	H	Fe	Per-centage homoan-nularity[l]
1[f]	IIIa	....	14900	66.61	5.10	27.79[e]	..
2[f]		....	7900	66.58	5.14	27.87[e]	61.6
3[g]		150/170[c]	4450	66.77	5.17	28.22[e]	67.1
4[h]		160[c]	2950	66.56	5.21	27.96[e]	71.0
5[i]		155	1700	66.85	5.08	28.11[e]	..
6[j]	IIIb	170/200[c]	9600	67.26	5.60	26.09	52.7
7[f]		165[d]	4650	67.78	5.91	26.27	58.6
8[k]		125/130	1960	68.18	5.78	26.32	75.6
9[g]		90/95	1060	67.99	5.85	26.15	80.0
10[h]		70/75	790	68.03	5.72	26.23	89.5
11[f]	IIIc	....	7500	74.14	5.31	20.15	37.0
12[f]		175[b]	4250	74.20	5.16	20.47	45.9
13[f]		165	2770	74.35	5.15	19.98	49.3
14[k]		140/145	1880	74.51	5.20	20.25	52.8
15[i]		125	1110	74.30	5.21	20.28	68.1

[a] Selected arbitrarily from several hundred fractions collected and analyzed. [b] See footnote 11. [c] Sintering only. [d] No clear melting. [e] Fe contents of high-molecular IIIa, as compared to IIIb and IIIc, frequently found 0.5–1.0% low; data presented here for IIIa are mean of two highest findings out of five repeats for each sample. [f] 1 hr. at 125°, 2% ZnCl₂. [g] 1 hr. at 120°, 1% ZnCl₂. [h] 1.5 hr. at 110°, 1% HCl. [i] 0.75 hr. at 110°, 1.5% ZnCl₂. [j] 1 hr. at 140°, 2% ZnCl₂. [k] 0.75 hr. at 115°, 0.8% AlCl₃. [l] Calcd. for IIIa: C, 66.71; H, 5.09; Fe, 28.20. IIIb: C, 67.96; H, 5.70; Fe, 26.34. IIIc: C, 74.48; H, 5.15; Fe, 20.37.

the bridging grouping –CH(R)–.[9] A characteristic medium-intensity band was exhibited in the 7.80 μ range by the polymers IIIa and IIIb. This absorp-

1,2-homo-   1,3-homo-   1,1'-hetero-

IIIa, R = H
b, R = CH₃
c, R = C₆H₅
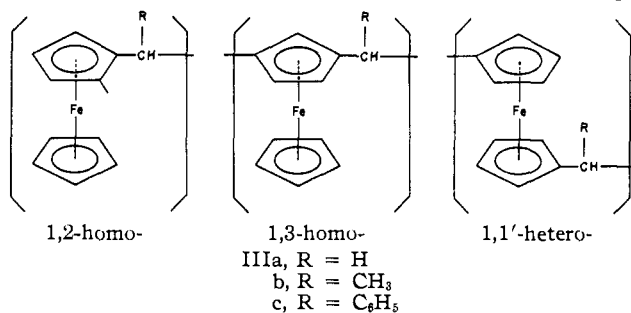
tion appears to be associated with a methylene or methine bridge of the mentioned type linking two ferrocene nuclei (possibly a twisting mode), the nature of R playing an important but as yet unclarified part.[10] While occurring with high intensity in diferrocenylmethane, it is absent, e.g., in 1,2-diferrocenylethane and di-(ferrocenylmethyl) ether. In the region near 10.80 μ, a medium-intensity band of variable position was exhibited by all polymers. While

(9) In IIIa, the broad CH₂ wagging absorption in the vicinity of 7.35 μ, sometimes resolved into a doublet, showed overlap with the previously reported ferrocene band in this region (ref. 2). A weak band at 10.60 μ, absent in IIIb and IIIc, may be assigned to a CH₂ rocking mode; it was enhanced in intensity as M_n increased. As in diferrocenylmethane, but in contrast to 1,2-diferrocenylethane, the CH₂ deformation band showed a shift to 7 μ. The tertiary CH grouping in IIIb and IIIc was evidenced by small peaks at 3.46 μ (stretching; in IIIb partially overlapped by the two strong stretching bands of the methyl group) as well as near 7.45 μ (bending; in IIIb frequently hidden in the broad absorption due to the methyl sym. bending mode). In the 14-μ region of CH bending variations due to the monosubstituted benzene system, IIIc showed a typical pattern of two bands near 14.0(s) and 14.3(m) μ, also exhibited by diferrocenylphenylmethane (ref. 10) and distinctly differentiated from absorptions in this region by ferrocenylphenylcarbinol or related ethers.

(10) The phenyl-bearing polymers IIIc as well as the monomeric model compound diferrocenylphenylmethane (infrared spectrum kindly submitted by Dr. N. Weliky, Jet Propulsion Laboratory, Pasadena, Calif.) fail to exhibit the 7.80-μ band. Only very weak absorption near 7.90 μ is shown (absent in 1,2-diferrocenyl-1,2-diphenylethane!) which, rather than attributable to the same vibrational mode as the discussed 7.80-μ band, must probably be ascribed to a phenyl absorption (cf. footnote 26 of the paper quoted in ref. 2).

near 10.85 μ in IIIa, it was shifted to 10.95 μ and 10.75 μ for IIIb and IIIc, respectively.

Polycondensations.—Of the polymer series discussed in this paper, the condensation products IIIa of hydroxymethylferrocene (IIa) showed the highest degree of polymerization, the number average molecular weights[7] ranging from approximately 2500 to 6000. On subfractions of sufficient monodispersity, M_n values in the range from ca. 1000 to 15,000 were measured. The fractionated polymers, with colors shifting from yellow to tan with increasing molecular weight, were readily soluble in such solvents as benzene, dioxane, N-methylpyrrolidone and chloroform, and poorly soluble in hexane and alcohols. With the exception of the lower members with $M_n < 3000$, the polymer was infusible and showed exceptionally strong adsorbability on activated alumina combined with an enhanced tendency toward oxidation while in the dissolved state. Samples changed by such oxidation showed a decrease in solubility and a color shift from yellow-tan to brown. Further aspects of the IIIa polymers are discussed in the Experimental section.

Polymers IIIb derived from (1-hydroxyethyl)-ferrocene (IIb) were in the molecular weight range 700–2000.[7] Upon fractionation, M_n values up to ca. 10,000 were attained. The lower members, when sufficiently monodisperse, showed defined melting ranges. A plot of m.p.[11] vs. M_n for such fractions is shown in Fig. 1 (lower curve). In extended investigations involving a large number of fusible, monodisperse fractions of this and other polymer series, relationships of this kind have proved valuable for characterization purposes, a simple melting point determination frequently providing a molecular weight assay with sufficient accuracy. The curve becomes meaningless for such evaluation, however, in the vicinity of the convergence temperature as well as in the oligomeric range (dinuclear through tetranuclear members), in which it is expected to pass through a minimum.

The roughly polyhomologous character of III was confirmed viscometrically, employing the series IIIb. In Fig. 2, using a log–log scale, the intrinsic viscosity, $[\eta]$, for a large number of fractions of the (1-hydroxyethyl)-ferrocene polymer is plotted against the number-average molecular weight, M_n. The graph shows that the $[\eta]$–M_n correlation, rather than obeying the Staudinger equation,[12] which has frequently been observed to hold for polymers in low molecular weight ranges, is of the Mark–Houwink type.[13] The following relation was established: $[\eta] = 3.95 \times 10^{-3} M^{0.27}$. The low exponent points to a branched, globular shape of the molecule, as also indicated by infrared analytical data to be discussed subsequently.

With α-hydroxybenzylferrocene (IIc), polymers IIIc were obtained with number-average molecular weights intermediate between the series IIIa and IIIb, i.e., in the 1800–3000 range[7] (upon fractionation, up to 10,000). When sufficiently monodisperse, the higher members, with M_n exceeding 4000, were no longer found to be clearly fusible. For the lower members, the m.p.–M_n correlation is represented by the upper curve in Fig. 1.

(11) In connection with polymer fractions throughout this paper, the m.p., defined as the upper limiting value of the melting range, denotes distinct fusing as indicated by a glossy surface of the sintered sample, coupled with wetting of the capillary wall. With well fractionated resins melting below 150°, the fused sample is usually reddish and transparent. As the m.p. rises above 175–180°, its clear-cut determination becomes increasingly difficult, thus rendering the findings meaningless for M_n assessment.

(12) H. Staudinger and W. Heuer, Ber., **63**, 222 (1930); **63**, 721 (1930); modified for low molecular polymers, e.g., by R. Fordyce and H. Hilbert, J. Am. Chem. Soc., **61**, 1912 (1939).

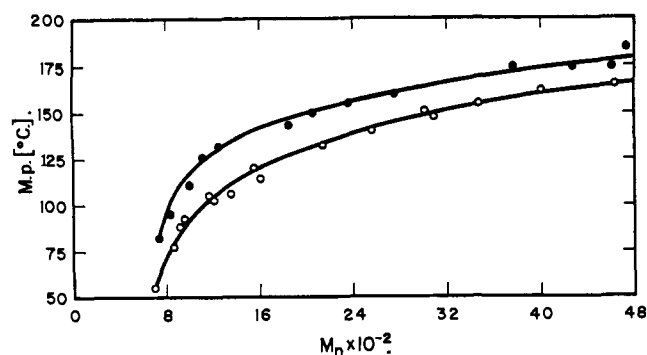(13) H. Mark, "Der feste Körper," Leipzig, 1938, p. 103; R. Houwink, J. prakt. Chem., **157**, 15 (1940).

Fig. 1.—Melting point[11] vs. number-average molecular weight: upper curve, polymer IIIc; lower curve, polymer IIIb.
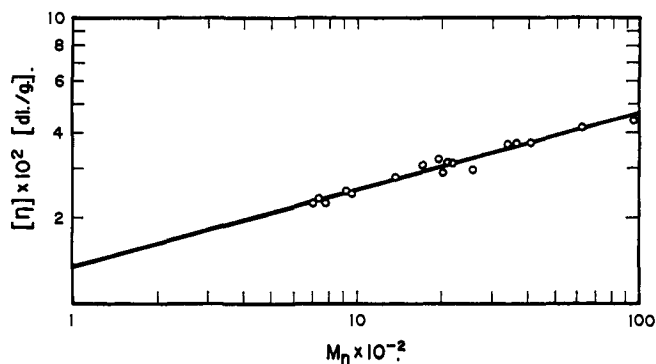

Fig. 2.—Intrinsic viscosity vs. number-average molecular weight for polymer IIIb.

Reaction conditions and results of the various runs are summarized in the Experimental section.

Polymer Structure.—Study of the substitution pattern of the recurring chain units with respect to homoannular and heteroannular substitution, as represented by the three segment structures III, was made possible by utilization of the valuable 9–10 μ rule,[14a,b] absorption at these two wave lengths being indicative of an unsubstituted π-cyclopentadienyl ring and absence of one or both absorptions pointing to substitution of both rings.

The existence of homoannular linkages in all three polymer series, IIIa, IIIb, and IIIc, was evidenced by the presence of the two strong bands in the vicinity of 9 and 10 μ. To determine the proportion of the two competing substitution orientations (homoannular vs. heteroannular) on the two ferrocene rings, a quantitative measurement[15] of the intensity of the 9-μ band was made on a large number of fractions. The procedure employed here is described in the Experimental part. The percentage homoannularity, i.e., the ratio, in per cent, of the experimentally determined number of unsubstituted π-cyclopentadienyl rings to the total number of ferrocene nuclei per molecule, is listed in the last column of Table I for the given polymer fractions.

The data permit interesting insight into some factors that influence the substitution behavior, under Friedel–Craft conditions, of ferrocene nuclei incorporated in polymer chain structures as compared to the general behavior of the ferrocene nucleus under normal, non-polymeric substitution conditions.[14b,16–18] Among reactions of the latter type, the acetylation of ethylferrocene,[14b] for instance, has revealed a ratio of the partial rate factors of 1.0:1.4:4.2 for the three nonequivalent relative positions, 1,1′-heteroannular:1,2-homoannular:1,3-homoannular, respectively. With statistical corrections resulting from the unequal number of these respective sites taken into account, these rate factors correspond to actual product proportions of 31% 1,1′-heteroannular, 17% 1,2-homoannular, and 52% 1,3-homoannular acetylethylferrocene, i.e., 69% over-all homoannular substitution. As can be seen from Table I and Fig. 3, the per cent content of homoannularly substituted ferrocenylene links in the present polymers matches these findings rather closely when taking into consideration the contrasting metallocarbonium cationic species and reaction conditions involved, as well as the additional
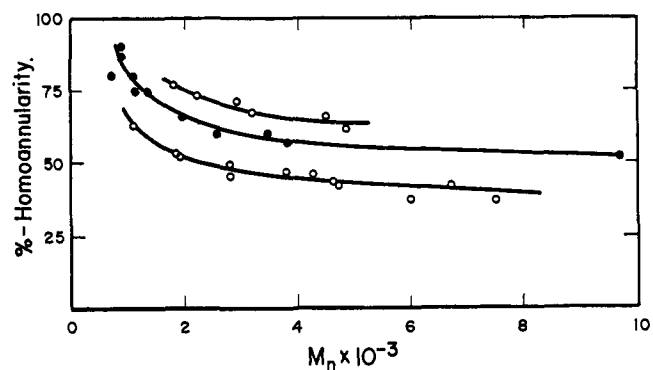

Fig. 3.—Percentage homoannularity vs. number-average molecular weight: upper curve, polymer IIIa; center curve, polymer IIIb; lower curve, polymer IIIc.

steric effects expected to operate in these complex polymer systems. Consequently, agreement in homoannular composition between the two reaction systems is closest for the lower molecular polymer fractions, where the interfering effect of factors associated with longer polymer chains, such as branching, play only a minor part. An additional fact clearly revealed by the graphs in Fig. 3 is the specific influence on percentage homoannularity exerted by the various substituent groups R in the three polymer series investigated. For any given molecular weight or, more meaningfully, degree of polymerization (visualized by shifting the curves slightly further apart on the x-axis), the percentage of homoannular linkages decreases in the sequence IIIa > IIIb > IIIc. Most probably, this effect is due mainly to the increasing size of the bridging group exercising increased steric hindrance at the adjacent 2-homoannular position. By reducing subsequent electrophilic attack at this site, substitution is proportionately increased at the remaining 3-homo and 1′-hetero positions, with a net increase in the over-all amount of heteroannular structure.[19] This result may also be correlated with the substitution orientation data on the non-polymeric systems, 1,1′-dimethylferrocene, 1,1′-diisopropylferrocene[16] and ethylferrocene,[14b] where a twofold increase in the ratio of 3- to 2-homoannular substitution in the sequence methyl, ethyl,

(14) (a) M. Rosenblum, Ph.D. Thesis, Harvard University, 1953; (b) M. Rosenblum and R. B. Woodward, J. Am. Chem. Soc., **80**, 5443 (1958).

(15) S. I. Goldberg and D. W. Mayo, Chem. Ind. (London), 671 (1959).

(16) K. L. Rinehart, Jr., K. L. Motz and S. Moon, J. Am. Chem. Soc., **79**, 2749 (1957).

(17) M. Rosenblum, ibid., **81**, 4530 (1959).

(18) Reference 2. The special substitution orientation exhibited by the arylcarbinyl substituents in this earlier investigation will be the subject of a later study.

(19) A. N. Nesmeyanov, L. A. Kazitsyna, B. V. Lokshin and V. D. Vilchevskaya, Doklady Akad. Nauk S.S.S.R., **125**, 1037 (1959), report 1,3-disubstituted ferrocene compounds to show infrared absorption near 7.80 μ. However, the presence of absorption at this position in IIIa and IIIb and its absence in IIIc, inconsistent with this correlation, appears not to constitute evidence relevant to homoannular orientation distribution in these polymers and was consequently interpreted above in a different manner. It should be noted in this connection that many monosubstituted ferrocene derivatives, including diferrocenylmethane as well as a number of heteroannularly disubstituted compounds, are known to absorb in the same region. Cf. M. Rosenblum and W. G. Howells, J. Am. Chem. Soc., **84**, 1167 (1962), and ref. 11 therein.

isopropyl was similarly interpreted as a neighboring steric effect.

In addition to the steric factor operative in effecting these expected results, some small degree of inductive homoannular deactivation by the phenylferrocenyl-carbinyl substituent in the IIIc polymer may contribute to increased hetero *vs.* homo substitution orientation.[20]

The dependence of the percentage of homoannular substitution on molecular weight for all three series of polymer fractions, as represented in Table I and Fig. 3, may also be interpreted consistently. From the high percentage homoannularity of lowest molecular weight fractions and the evidence cited above on steric substitution effects at adjacent homoannular sites, it may be expected that initially formed polymer would have homoannular linkages of predominantly the 1,3-type. Except for chain ends, which become less accessible with increasing molecular weight, such 1,3-linked polymer has no remaining sterically unhindered homoannular sites for further substitution, the two potential sites in the sterically favored 3-position with respect to one arm of the polymer being 2-situated with respect to the other. As the concentration of chain ends decreases with increasing molecular weight, the statistical probability for linear propagation falls and further substitution must increasingly occur on the unhindered hetero ring of random chain segments, resulting in branching. Through the quantitative infrared analytical method employed, this branching growth is reflected as a decreasing over-all homoannularity: heteroannularity trend. The observed approach to respective convergence values with increasing molecular weight (Fig. 3) occurs as a steady state is attained, the growth process becoming balanced between initiation of branches and their early-stage linear growth.

In this connection it should also be noted that while polymer segments initially linked homoannularly lose their 9–10 μ infrared detectability (and, hence, evidence of original homoannular structure) during subsequent branching substitution on their hetero rings, initially formed heteroannularly-linked segments remain unaffected spectroanalytically by later branching reactions.

Polymerization Reactions.—Viewed in greater generality, the several reaction paths concurrently available to the generated carbonium ions in terms of carbon chain growth include (1) rapid reaction with the various ROH species to yield corresponding ethers (no growth), (2) nuclear substitution of alcohol or ether species (growth), (3) nuclear substitution of oxygen-free polymer (growth), (4) self-substitution on penultimate nucleus (no growth). At the early reaction stage, steps 1 and 2 must predominate, but as dehydration proceeds and alcohol and ether intermediates increase in molecular weight and decrease in concentration, resulting carbonium ions will react progressively *via* steps 3 and 4 until ionization and conversion of polymeric alcohols and ethers to oxygen-free metallohydrocarbon polymer is essentially complete.

Although direct evidence for reaction 4 above is not experimentally accessible, such an intramolecular reaction step is both readily predictable and at the same time necessary to account for the generally limited molecular weight of the final reaction products, since it represents the only irreversible non-growth termination reaction in the above set of available reaction paths. The remaining two nuclear substitution reactions 2 and 3 are both growth steps, and the final molecular weight is a function of the over-all rate ratio between these competitive growth and non-growth reactions. Of the

(20) See in this connection ref. 17.

three linear chain orientations, only the 1,2-homoannular and 1,1'-heteroannular cations can self-substitute on their penultimate nuclei, the 1,3-homoannular cation having an impossible geometry for such a non-growth step.[21]

Taking this fact into account and considering the expected ratios and reaction probabilities of these three orientations, an interpretation of the sequence of molecular weight ranges obtained for the three classes of polymers (IIIa, b, c) can be suggested. In all probability, the extent to which the four competing reaction steps are subject to the structural influence of R in these three polymer classes is predominantly determined by the relative reaction rates of their 1,2-homoannular cations. For the IIIa polymer cation, earlier noted to show the highest degree of homoannular and therefore 2-homo substitution, the self-addition sites at the required 2-homoannular position of the penultimate link will be correspondingly less available, thus increasing the probability of intermolecular growth steps and, hence, high molecular weights. In these same terms, the phenyl group of IIIc could offer sufficiently more steric hindrance to the penultimate 2-homoannular position compared to methyl (IIIb) and, hence, similarly favor reactions 2 and 3 over 4, so that the molecular weight sequence IIIa > IIIc > IIIb would then result as observed.

Experimental[22]

Reagents and Starting Materials.—Solvents employed were reagent grade (spectrograde for infrared work). Anhydrous aluminum chloride, resublimed, was used as received. The commercially available anhydrous zinc chloride was further dried by heating for several hours above the melting point; the salt, while still hot, was ground and bottled under dry nitrogen. The activated alumina was Alcoa grade F-20.

Hydroxymethylferrocene was prepared as described[23] and was purified chromatographically in hexane solution; m.p. 80° (hexane). (1-Hydroxyethyl)-ferrocene was obtained by sodium borohydride reduction of acetylferrocene in 20:80 dioxane-ethanol solution; m.p. upon chromatographic purification and recrystallization from hexane, 78–80° (lit.[24] 73–75°). In an analogous procedure, α-hydroxybenzylferrocene was prepared from the corresponding benzoyl derivative; m.p. 80–81°. The method described by Hauser[25] was employed to synthesize di-(ferrocenylmethyl) ether; chromatography and recrystallization from hexane yielded a product, m.p. 132–132.5°.

Polycondensation Reactions.—Except for minor modifications, the technique applied was basically the same for all polycondensations performed. The well ground mixture of ferrocenylcarbinol derivative and catalyst in the specified concentration,[5] with total batch sizes ranging from 5 to 20 g., was placed into a round-bottom flask equipped with a mechanical stirrer. Two side tubes attached to the upper part of the flask allowed for a slow stream of dry nitrogen to be passed over the mixture throughout the reaction to prevent air oxidation and facilitate removal of condensation water. The mass was heated with stirring in an oil-bath under conditions of time and temperature as specified below for the individual experiments. In two cases, the intermediate ethers were isolated during the initial phase. Unless otherwise stated, heating was continued to the point of maximum conversion, which usually attained when the melt had assumed a high viscous, resinous consistency rendering further stirring difficult. The cold, brittle melt was ground and briefly washed with methanol.[26] The dried resin was dissolved portion-

(21) Unless heteroannularly branched at that point.

(22) All temperatures given in degrees centigrade; melting points uncorrected, taken up to 300°. Infrared spectra recorded from solution in CCl₄ (2–7.5 μ) and CS₂ (7–15 μ), using a Perkin–Elmer, model 21, double-beam spectrometer equipped with rock salt optics; cell thickness 0.1 cm. Number-average molecular weights by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., using a Mechrolab vapor pressure osmometer; all measurements *in duplo* in benzene solution, rounded off to nearest 10 for M_n up to 3000; to nearest 50 for M_n up to 6000; to nearest 100 for $M_n > 6000$. Fe analyses by the same laboratory; C, H analyses by G. I. Robertson, Jr., Florham Park, N. J.

(23) J. K. Lindsay and C. R. Hauser, *J. Org. Chem.*, **22**, 355 (1957).

(24) F. S. Arimoto and A. C. Haven, Jr., *J. Am. Chem. Soc.*, **77**, 6295 (1955).

(25) C. R. Hauser, *J. Org. Chem.*, **23**, 2007 (1958).

(26) In reactions prematurely discontinued, starting materials as well as monomeric ethers were extractable by this operation.

wise in a total of 60–80 ml. of dioxane for each 10 g. of solids and was reprecipitated by stirring the filtered solution dropwise into the fourfold volume of 95% aqueous methanol. Upon filtering and drying *in vacuo*, the crude polymer was obtained as a dirty yellow powdery solid. With low molecular polymers, a small second crop, sometimes resinous, was collected from the mother liquor by addition of excess water. The total crude yield of vacuum-dried product amounted to 85–96%.[27] To remove traces of polymeric oxidation products and some residual polymeric ethers, a benzene solution of the polymer was rapidly passed through a small chromatographic column packed with activated alumina (for high-molecular IIIa, grade F-20 alumina was partially deactivated by allowing it to stand for 20 hr. in contact with the open air). The material recovered from the benzene eluate was then fractionally precipitated in the conventional manner from benzene solution at $25 \pm 0.5°$ in a thermostatically controlled water-bath, using methanol and, finally, aqueous methanol as the precipitants. The operation was carried out following the customary pattern of redissolving and reprecipitating each fraction and adding the second filtrate to the main mother liquor prior to the subsequent precipitation step. In order to render the final fractions precipitable in a two-phase system without excessive volume increase, the mother liquors had to be partially evaporated. All crude resinous fractions were digested with cold methanol and dried for 48 hours at 50° *in vacuo* for yield determination. They were reprecipitated from dioxane solution in the manner initially described and vacuum-dried for 1 week at a temperature sufficiently below the melting range to prevent sintering. The average number of fractions thus isolated amounted to 15 (in several instances, as individually mentioned, cruder fractionations were carried out resulting in a smaller number of less monodisperse fractions). Not included in this figure and disregarded as an analyzable fraction was the final portion of solids obtained by evaporation to dryness of the concentrated mother liquor. In general, it did not exceed 5% of the total polymer and constituted a multi-component mixture probably comprising residual ethers as well as oxidation products which had lost their full solubility in benzene. To minimize loss by oxidation, peroxide-free dioxane was employed and all filtrations were done with highest feasible speed. For more precise work, use of deaerated solvents and precipitants and nitrogen blanketing of all operations would be additionally advisable.

Unless specifically stated to the contrary, essentially identical elemental compositions were found for all individual fractions within a given polymer series. For fractions in the same molecular weight range, also, the spectroscopically determined homoannular contents (see below) were comparable within the limits of experimental reproducibility.

The fractionated polymers were infinitely soluble in such solvents as benzene, dioxane, N-methylpyrolidone and chloroform. They were insoluble in water and practically so in hexane and aliphatic alcohols. Only the low members showed solubility in dimethylformamide (with IIIc, also higher members) and to a slight extent in hexane and alcohols. All polymers were electrostatically chargeable; very brittle films could be cast from melt or solution.

Condensation of Hydroxymethylferrocene (IIa); Formation of IIIa. (a) With ZnCl$_2$ as Catalyst.—At 90° oil-bath temperature and 1% catalyst concentration, the starting material formed a uniform melt which soon solidified to an orange-brown crystalline mass essentially constituting di-(ferrocenylmethyl) ether (in a parallel experiment, the total crude yield of the ether was found to be 91%). A sample of this intermediate was twice recrystallized from hexane to afford orange prisms, m.p. 132°; on admixture with authentic product, no depression. To allow the ether to remelt, the bath temperature was briefly raised to 130° and was then maintained for approximately 1 hour at 110° until blocking of the stirrer occurred. The reaction product was worked up as previously described to give crude polymer in 93% yield, partially melting at 130–150°; M_n of unfractionated resin, 3450.

Anal.[28] Calcd. for IIIa: C, 66.71; H, 5.09; Fe, 28.20. Found: C, 66.84; H, 5.21; Fe, 27.90.

By fractional precipitation, 13 fractions were isolated with M_n values of the major portion (all center fractions approximating one-half the total weight) falling within the range 2500–5000. The last (lowest) fraction (M_n 1250), without substantially deviating in elemental composition, showed weak infrared absorption at 7.50–7.60 μ and near 9.30 μ as exhibited by the monomeric ether. Representative fractions of this and the following experiments are listed as no. 1 through 5 in Table I. It should be noted that, in order to obtain analytical findings as listed,

in particular on high molecular fractions, the above-mentioned precautions to prevent oxidation had to be strictly observed. Fractions isolated under less careful conditions showed average reductions of the C and Fe contents by as much as 0.5–1.0%.

With 2% ZnCl$_2$ and the bath temperature maintained at 135–140° throughout the reaction, the condensation was substantially completed within 25 min. The crude polymer (yield 96%) began to sinter at 150–170°, M_n 4500, % homoannularity 63.8; M_n range of major portion of subfractions with over-all weight approximating 50% of total, 4000–8000. An experiment conducted for comparison at the same temperature, but with the ZnCl$_2$ concentration increased to 20%, was completed within 5 min. The crude polymer, obtained in 91% yield, had M_n 5600 (no subfractionation performed). A polymer of practically identical composition resulted from condensation of the corresponding di-(ferrocenylmethyl) ether in place of the carbinol.

(b) With Hydrochloric Acid as Catalyst.—The catalyst, 1% HCl employed as a 10% aqueous solution, was stirred homogeneously into the powdered carbinol. Total heating time was 80 min., the bath temperature being 130° during the initial step of ether formation and 110° for the polycondensation phase proper. The crude polymer, partially melting at 110–130°, M_n 2850, was obtained in 86% yield. It was further subdivided in 5 fractions only; the second fraction, constituting nearly one-half the total weight, showed beginning melting at 150°, M_n 3550, % homoannularity 71.3. The last fraction, partially melting at 100–125°, M_n 980, exhibited ether bands at 7.50–7.60 μ and near 9.30 μ.

(c) With AlCl$_3$ as Catalyst.—Applied in a concentration of 1%, this catalyst required approximately 1-hr. reaction time at 110° to give crude, tan-colored polymer in 87% yield, partially melting near 200°, M_n 5200 (no low molecular members formed). Coarsely subfractionated, it afforded 4 tan-colored fractions of decreased solubility in CS$_2$, sintering between 150 and 200°. The elemental compositions were essentially identical with those reported above, except for the presence of oxygen ranging from 1% in the last, to as much as 4.8% (by difference) in the first fraction. The second fraction, M_n 7450, was analyzed. C, 65.08; H, 5.18; Fe, 25.97; balance (by difference), 3.77; % homoannularity, determined on CS$_2$-soluble portion of this fraction, 87.5. When passed in concentrated benzene solution through a short column packed with activated alumina, only *ca.* 45% of the original fraction was recoverable; after reprecipitation from dioxane solution into excess methanol, it formed a brown, fine-powdery, infusible solid.

Anal. Found: C, 63.98; H, 4.96; Fe, 24.22; balance (by diff.), 6.84.

The polymer portion retained on the carrier could to a very small extent be eluted by such solvents as dioxane or dioxane-methanol blends. Elemental analysis performed on the dark-brown brittle solid exhibited a further decreased metallohydrocarbon content (balance *ca.* 7.5%), probably as a result of preferential adsorption of polymeric fractions containing more polar sites. Decreased solubility in the standard solvents, especially in CS$_2$, was correspondingly observed.[29]

Condensation of (1-Hydroxyethyl)-ferrocene (IIb); Formation of IIIb.—Reaction conditions and results of the various runs employing this carbinol are summarized in Table II. Five typical polymer fractions are listed in Table I. For the low members of IIIb, particular care had to be exerted in washing and drying to prevent early sintering induced by traces of included solvent. The intermediate ether compound, di-(1-ferrocenyl-ethyl) ether, was isolated in one experiment; upon repeated recrystallization from hexane, it formed orange needles, m.p. 82–83°. Besides the absorption typical of the substituted ferrocene and methyl groups, the infrared spectrum showed strong ether bands, variable in position, at 7.70 μ and 9.0–9.25 μ (the latter as doublet overlapping the 9-μ ferrocene band). In addition, a medium intensity band was noticed as a shoulder at 8.95 μ.

Anal. Calcd. for C$_{24}$H$_{26}$OFe$_2$: C, 65.19; H, 5.93; Fe, 25.26. Found: C, 65.03; H, 6.10; Fe, 25.04.

The viscosities for Fig. 2 were measured in benzene solution at $25 \pm 0.05°$, using a Manning–Fenske type viscometer and applying kinetic energy corrections. The intrinsic viscosity, $[\eta]$, was determined in the conventional manner by extrapolating the plots of reduced viscosity *vs.* concentration to zero concentration. The spread of some of the points may be due to deviation from strictly polyhomologous structure as also evidenced elsewhere.

(27) With duplicate runs, yields are given as rounded-off mean values.

(28) In the majority of runs, the crude polymer was analyzed for C, H and Fe content as in the present instance. In view of consistent findings here as well as for fractionated samples, analytical data are not specifically listed in the following experiments.

(29) Formation of these impure polymer fractions obtained from hydroxymethylferrocene (IIa) with AlCl$_3$ may be due to increased coupling of pairs of cations (I, with polymeric nuclear substituent, and R = R' = H), resulting from the highest $\delta+$ charge on Fe and highest methylene radical character of the three cation types investigated, with AlCl$_3$ aiding by providing higher cation concentration. Resulting ferricinium ion sites with their associated anions, inconspicuous in the predominantly neutral polymer, could account for the various observations above.

TABLE II

Polymer series	Concn.[a] and type of catalyst	Bath temp., °C.	Time, min.	Yield[b] of crude polymer, %	M_n[c] of crude polymer	Melting-range of crude polymer, °C.	Approx. M_n range of major portion of center fractions[d]
IIIb	1% $ZnCl_2$	120	60	91	1210	80–95	1000–2100
	2% $ZnCl_2$	120	30	86[e]	1100[e]	75–100[e]	1200–2500[e]
	2% $ZnCl_2$	140	60	93	1370	85–105	1200–3500
	10% $ZnCl_2$	140	10	90	1990	100–130	1300–3900
	0.7% $AlCl_3$	120	60	87	1120	80–110	900–2200
	1% HCl	110	40	87[f]	790	50–90	800–1400
IIIc	1.5% $ZnCl_2$	120	60	93[g]	2180	120–150	1900–4000
	1.5% $ZnCl_2$	125	180	94	2500	120–155	2200–5000
	3.2% $ZnCl_2$	125	180	89	3000	135–170	2500–5000
	5% $ZnCl_2$	120	20	92	2120	110–145	1500–3000
	1% $AlCl_3$	100	40	86	2730	135–165	2500–5000
	1.5% HCl	125	180	85[g]	1910	100–135	1600–2800

[a] See ref. 6.   [b] See ref. 27.   [c] See ref. 7.   [d] All center fractions totaling approximately one-half the over-all polymer weight after fractionation.   [e] Essentially the same results with corresponding diether in lieu of carbinol.   [f] Last 2 fractions exhibit ether bands.   [g] Last fraction exhibits weak ether bands.

Condensation of α-Hydroxybenzylferrocene (IIc); Formation of IIIc.—The experimental details are given in Table II. Five characteristic polymer fractions are recorded in Table I. In
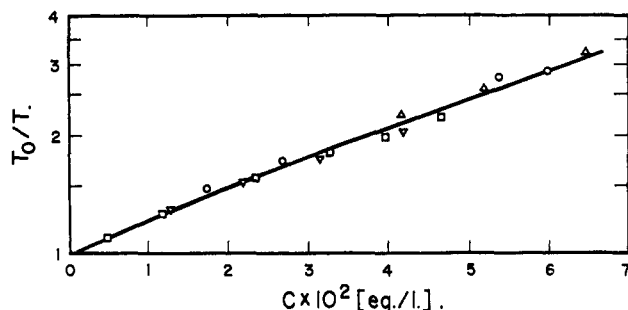

Fig. 4.—Intensity ratio T_0/T of the 9-μ band vs. equivalent concentration of unsubstituted π-cyclopentadienyl rings: O, ferrocene; □, triphenylmethylferrocene; ▽, 1,2-diferrocenylethane; △, diferrocenyl.

contrast to IIIa and IIIb, even fractions with M_n as high as 6000 proved to be soluble in dimethylformamide. Also, a diminished tendency of the low members toward sintering was noticed, facilitating their isolation in powdery form.

Determination of Percentage Homoannularity.—In Fig. 4, for several known homoannular ferrocene compounds, the intensity ratio for the 9-μ band, $(T_0/T)_{9\mu}$, is plotted on a semilogarithmic paper against the respective concentration, C, in equivalents of unsubstituted π-cyclopentadienyl rings per liter of solution. T_0 and T, the apparent[30] intensities of the incident and transmitted radiation, respectively, were determined at 25 ± 1° in CS_2 solution, employing the base-line method of Heigl, et al.[31] The path length was 0.10 cm. To obtain the percentage homoannular content (% homoannularity) of a polymer of unknown substitution pattern, the T_0/T ratio was determined by the same procedure as above, applying a polymer concentration such as to confine the numerical value of T_0/T within the range from ca. 1.3 to 2.5. For this ratio, the pertinent equivalent concentration, C, was read off the curve in Fig. 4. This found value of C, divided by one-hundredth the actually applied polymer concentration expressed as equivalents of ferrocene units per liter, provided the per cent content of homoannularly-linked ferrocene nuclei (% homoannularity) in the given polymer fraction.

The method was checked on a number of monomeric ferrocene derivatives containing unsubstituted rings and was found to hold with an average deviation of ±6% for all compounds investigated except those bearing carbonyl, ether or other polar groups, for which a greater deviation occurred.

(30) Terminology chosen in accordance with D. A. Ramsay, J. Am. Chem. Soc., 74, 72 (1952); cf. also R. N. Jones, et al., ibid., 74, 80 (1952), and R. R. Hampston and J. E. Newell, Anal. Chem., 21, 914 (1949).

(31) J. J. Heigl, et al., ibid., 19, 293 (1947). While its weaknesses are well recognized, this method was chosen for simplicity, its accuracy and reproducibility being sufficient for the present purpose.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CASE INSTITUTF OF TECHNOLOGY, CLEVELAND 6, OHIO]

The Decomposition of Peroxides Catalyzed by Copper Compounds and the Oxidation of Alkyl Radicals by Cupric Salts[1]

BY JAY K. KOCHI

Diacyl and dialkyl peroxides, peresters and alkyl hydroperoxides as classes of peroxides are catalytically decomposed by copper salts in non-aqueous solutions. It is demonstrated that the decomposition is initiated by the one-electron reduction of the peroxidic bond by cuprous salt to form cupric species and oxy free radicals, which yield alkyl radicals on fragmentation. Cuprous catalyst is regenerated by the subsequent cupric oxidation of the alkyl free radicals. The catalysis is inhibited by halogens which readily oxidize cuprous salts. The oxidation of the isomeric butyl radicals exclusively to butenes occurs with no skeletal rearrangement. The approach to statistical distribution of butene-1 and trans- and cis-butene-2 from the oxidation of sec-butyl radicals is discussed. Neopentyl radicals are not as efficiently oxidized as those radicals which possess a β-hydrogen and products of rearrangement are obtained. The mechanism of the oxidation of alkyl radicals by simple and complex copper salts is discussed.

Introduction

Substitution reactions effected by peroxides in the presence of metal salts such as copper, cobalt and manganese have been described by Kharasch and co-

workers.[2] These reactions are given by eq. 1 in which a hydrogen donor (RH) undergoes a metathetical re-

$$XOOY + RH \xrightarrow{Cu^{+n}} XOH + ROY \qquad (1)$$
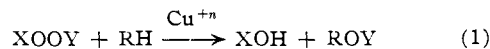
(1) (a) Part VI. Reactions of Peroxides Catalyzed by Metal Salts. Part V: J. Am. Chem. Soc., 84, 3271 (1962).   (b) Presented in part at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 13, 1962.

(2) M. S. Kharasch and A. Fono, J. Org. Chem., 23, 324 (1958); 24, 606 (1959); M. S. Kharasch, G. Sosnovsky and N. C. Yang, J. Am. Chem. Soc., 81, 5819 (1959); G. Sosnovsky and N. C. Yang, J. Org. Chem., 25, 899 (1960).