

from the intensity of the carbonyl absorption at 1670–1715 cm^{-1} in the infrared.

In those runs in which phenylorganometallic reagents were employed, the products were chromatographed on neutral alumina, unreacted bromobenzene and biphenyl being eluted with pentane, and product being eluted with ethyl acetate.

Starting ketone was removed with Girard reagent by a method previously recorded¹⁵ in those runs whose product showed carbonyl absorption. In those runs which involved 2,3-diphenyl-3-hydroxy-2-butanone as starting material, this method failed to remove starting material. These products were reduced with excess lithium aluminum hydride, and careful chromatography of the product on neutral alumina allowed separation of the secondary and tertiary alcohols. The latter was eluted with a 25:75% mixture of ethyl acetate–ether. Control runs established the reliability of this method of separation.

Reactions Leading to 2,3-Diphenyl-3-methoxy-2-butanols.—These reactions were conducted identically to those leading to the 2,3-diphenyl-2,3-butanediols except that the appropriate methoxy ketones were substituted for the hydroxy ketones. After the carbonyl compound was added to the organometallic, the reaction mixture was stirred for 1.5 hr. The yields of these reactions were estimated from the intensity of the carbonyl absorption of the products at 1715 cm^{-1} for reactions involving (\pm)-3-methoxy-3-phenyl-2-butanone and at 1680 cm^{-1} for reactions with (\pm)-1,2-diphenyl-2-methoxy-1-propanone as starting material.

Analysis of Diastereomers.—The mixture of diastereomers produced when 2,3-diphenyl-2,3-butanediol was product was analyzed by the method developed earlier.⁴ Results of comparable internal consistency were obtained in this as in the previous investigation.⁴

The mixtures of diastereomers of 2,3-diphenyl-3-methoxy-2-butanol produced were analyzed as follows. The *threo* isomer possessed infrared spectral bands at 1353, 1191, 1151 and 1059 cm^{-1} which were not present in the *erythro* isomer. The spectrum of the *erythro* isomer did not possess any bands not present in the *threo* isomer. Thus the 4 bands of the *threo* isomer were used in the analysis.

(15) D. J. Cram and J. E. McCarty, *J. Am. Chem. Soc.*, **79**, 2872 (1957).

TABLE VI

INFRARED ANALYSIS^a OF PERCENTAGE DIASTEREOMERIC MIXTURES OF 2,3-DIPHENYL-3-METHOXY-2-BUTANOLS^b

Run	1353	1191	1151	1059	Average	
	cm^{-1} <i>threo</i>	cm^{-1} <i>threo</i>	cm^{-1} <i>threo</i>	cm^{-1} <i>threo</i>	<i>threo</i>	<i>erythro</i>
38	39	38	22	35	33	67
39	43	38	28	37	37	63
40	72	71	67	69	70	30
41	44	41	52	44	45	55
42	45	43	51	50	47	53
44	83	89	89	87	87	13
45	82	88	88	86	86	14
46	89	95	93	93	93	7
47	91	96	97	95	95	5
48	90	95	95	90	93	7

^a A Perkin–Elmer model 21 recording spectrophotometer, sodium chloride prism, cell thickness 0.096 mm., was used.
^b Amount of *erythro* in mixture equals 100% – % *threo*.

The samples (oils) to be analyzed were heated as a film to 80° for 1 hour at 1 mm. to remove the last traces of solvent. The oils (1.000 g.) were dissolved in 15.00 g. of carbon tetrachloride. Standard solutions of the same concentration of pure *threo* and *erythro* isomers were prepared, as well as four synthetic mixtures (1:4, 1:2, 1:1, 2:1, 4:1). The absorption band at 1450 cm^{-1} for both *threo* and *erythro* isomers was used as an internal standard. Spectra of the known and unknown samples were taken and all spectra were normalized to an absorbance of 0.452 at 1450 cm^{-1} . The corrected optical densities of the known mixtures at the 4 different wave lengths were plotted against the % composition. The compositions of the unknowns were then read from the graphs. An average of the values at the 4 different wave lengths was taken to be the correct value for the unknowns. The results are recorded in Tables VI, III and IV.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES, LOS ANGELES 24, CALIF.]

Studies in Stereochemistry. XXXIII. Approaches to Models for 1,3-Asymmetric Induction¹

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Systems have been investigated that might serve as models for 1,3-asymmetric induction in the anionic polymerization of olefins. Measurement of the *erythro*/*threo* ratio in the production of III from I and II was conceived as a model for isotactic polymerization. The ratio of *threo*/*erythro*-VII in the addition of V to VI might serve as a model for syndiotactic polymerization. Addition of I to II failed because of intervention of an elimination reaction of I to give propene and the products of reactions of the 9-methyl-9-methylfluorenyl anion. Organometallic compound V failed to add to VI. Both diastereomers of VIII were prepared and their configurations determined. The ratio of diastereomers formed by addition of carbon dioxide and formaldehyde to V was measured and found to be independent of which diastereomeric bromide served as starting material for preparation of the Grignard reagent. The *erythro*/*threo* ratio of products varied from 1.27 to 1.12. This result is interpreted as reflecting the ratio of diastereomeric Grignard reagents initially formed rather than the relative energies of the transition states for the addition reactions. "Paper models" for stereospecific anionic polymerization are discussed.

One of the more challenging stereochemical problems of current interest involves development of an understanding of why certain polymerization reactions produce configurationally ordered chains which contain asymmetric centers at regular intervals. Most of these polymerizations involve addition reactions to carbon-carbon double bonds to give asymmetric centers 1, 3 to one another. Mechanisms available for rationalization of the observed stereoregularity fall into three classes: (1) those which place a stereochemical memory at the very end of each growing chain in the form of asymmetric catalytic sites³; (2) those which invoke 1,3-asymmetric induction in the formation of each new asymmetric center⁴; (3)

those which point to asymmetric induction and involve sites further down the chain than the last asymmetric center.^{4a,5}

This paper reports the results of an attempt to find reactions which would allow an experimental evaluation of the magnitude of effects in 1,3-asymmetric induction. The reaction, I + II \rightarrow III, was conceived as a possible model for isotactic, and V + VI \rightarrow VII for syndiotactic, polymerization. These reactions were selected for two reasons. (1) Analogies for these addition reactions were available in the literature.⁶ (2) The relative configurations of the diastereomers of III and VII could be determined through use of the

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(2) N.S.F. Predoctoral Fellow, 1959–1961.

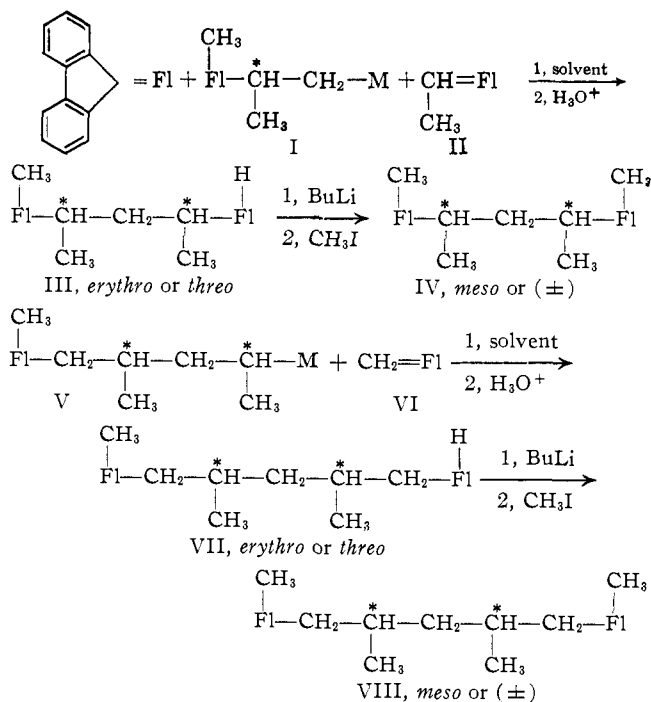
(3) (a) G. Natta, P. Pino and G. Mazzanti, *Gazz. chim. ital.*, **87**, 528 (1957); (b) C. M. Fontana and R. J. Osborne, *Polymer Sci.*, **47**, 522 (1960); (c) P. Cossee, *Tetrahedron Letters*, **17**, 12, 17 (1960).

(4) (a) D. J. Cram and K. R. Kopecky, *J. Am. Chem. Soc.*, **81**, 2748 (1959); (b) J. Furukawa and T. Tsuruta, *Polymer Sci.*, **36**, 275 (1959); (c) G. I. Fray and R. Robinson, *Tetrahedron*, **18**, 261 (1962).

(5) (a) D. J. Cram, *J. Chem. Ed.*, **37**, 317 (1960); (b) W. E. Goode, F. H. Owens and W. L. Meyers, *J. Polymer Sci.*, **47**, 75 (1960).

(6) (a) K. Ziegler, F. Crossmann, H. Klein and O. Schafer, *Ann.*, **473**, 1 (1929); (b) R. C. Fuson and F. E. Mumfor, *J. Org. Chem.*, **17**, 225 (1952).

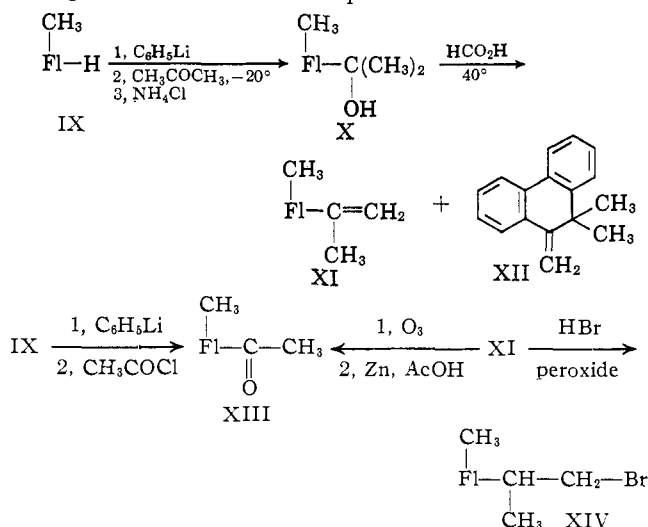
symmetry properties of their methylated products IV and VIII. The methyl groups were put in the 9-position of the fluorene nucleus in I and V to avoid internal metalation reactions.



Results

Starting Materials.—The two alkenes 9-ethylidene-fluorene (II)⁷ and 9-methylenefluorene⁸ were both unstable to light and air, particularly the latter compound, which is 200 times more susceptible to radical polymerization than styrene.⁸ They were prepared and stored *in vacuo* in a cold dark place.

Preparation of bromide XIV from 9-methylfluorene (IX)⁹ is formulated. At 0°, 9-lithio-9-methylfluorene abstracted a proton from acetone to give IX, whereas at -20°, the organometallic added smoothly to acetone to give X. At 0°, methyl lithium and ketone XIII also gave IX, but at -20° provided alcohol X.¹⁰



Apparently the lithium salt of alcohol X cleaves at 0° to give 9-methyl-9-fluorenyllithium, which abstracts a proton from acetone at that temperature.¹¹

(7) A. Pullman, B. Pullman, E. D. Bergmann, B. Berthier, Y. Hirshberg and Y. Sprinzak, *Bull. soc. chim. France*, [5] **18**, 702 (1951).

(8) J. R. Kice, *J. Am. Chem. Soc.*, **80**, 348 (1958).

(9) K. L. Schoen and E. I. Becker, *ibid.*, **77**, 6030 (1955).

(10) F. H. L. Anet and P. M. G. Bavin, *Can. J. Chem.*, **36**, 763 (1958).

(11) For analogies, see (a) P. M. G. Bavin, *ibid.*, **38**, 882 (1960), and (b)

A small amount of product of a Wagner–Meerwein rearrangement (XII) was observed in the dehydration of X. The spectral properties of compounds X to XIV were consistent with the structures drawn.

Three approaches (see formulas) to the synthesis of bromides XXVIII were made. The first of these proved impractical. Although alcohol XXII was obtained as a diastereomeric mixture, side reactions throughout the sequence accounted for too large an amount of the starting material. Phenanthrene derivative XVIII could have arisen by a twofold Wagner–Meerwein rearrangement with first hydrogen and then phenyl as migrating group. The substance was also formed in generous quantities when hydrogen bromide was added to alkene XVII. Compounds XIX, XX and XXI were all probably formed during the preparation of the Grignard reagent from XVI. The diastereomers of XXI proved separable by V.P.C. at high temperature.

The second approach failed because of the resistance of ketone XXVI to simple reduction. Conditions of the Clemmensen reduction resulted in a more rapid loss of the elements of acetic acid to give olefin than reduction of the carbonyl group.

Conditions of the Wolff–Kishner reduction provided a cleavage reaction of ketone XXVI to give 9-methylfluorene. The third approach, which proved successful, made use of the difference in reactivity toward a strong nucleophile (9-methyl-9-fluorenyllithium) exhibited by the bromide and tosylated groups in XXVII. One of the diastereomeric bromides of XXVIII was secured as a pure crystalline entity, whereas the other was only obtained in an enriched state.

Addition Reactions of 9-Ethylidene-fluorene.—Preparation of the lithium reagents of this study was greatly facilitated by use of lithium wire with an 0.8% sodium content¹² and an atmosphere of helium.¹³ Addition of *n*-butyllithium to 9-ethylidene-fluorene (II) in hexane could be detected by formation of the red color of the fluorenyl anion, and was found to occur only above 0°. At 25° in hexane, II was completely consumed by the organolithium reagent to give excellent yields of 2-(9-methyl-9-fluorenyl)-hexane. The same reaction occurred rapidly at -55° in ether to give similar results.

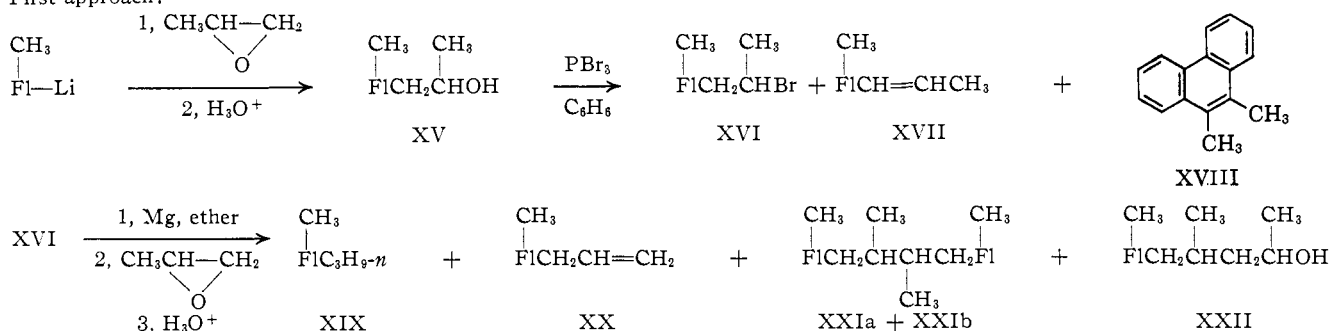
Formation of the lithium reagent from bromide XIV in hexane was possible only in the presence of *n*-butyllithium. Attempts to add this lithium reagent (XXIX) to 9-ethylidene-fluorene at 5–30° resulted in products which could have arisen only from 9-lithio-9-methylfluorene formed by an elimination reaction of XXIX. In ether solution, the organometallic reagent XXIX formed readily at -40° but largely precipitated from solution. No reaction between this reagent and 9-ethylidene-fluorene occurred in ether solution at temperatures between -55° and 25°. At 20°, XXIX again cleaved to give the products formulated. When titanium tetrachloride was added to XXIX below 0° and 9-ethylidene-fluorene then added, the same reactions occurred, but this time below 0°. Apparently the transition metal salt catalyzes the elimination reaction of XXIX. Thus the attempt to use the reaction between I and II as a model for isotactic polymerization failed due to decomposition of the organometallic reagent itself. Instead of the desired addition, an elimination reaction occurred. The stability of the 9-fluorenyl anion undoubtedly provides the driving force for this unusual elimination reaction.

D. J. Cram, J. L. Mateos, F. Hauck, A. Langemann, K. R. Kopecky, W. D. Nielsen and J. Allinger, *J. Am. Chem. Soc.*, **81**, 5774 (1959).

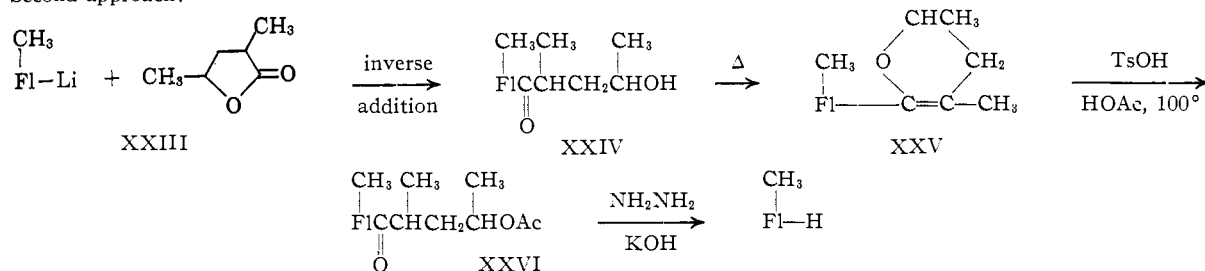
(12) C. W. Kamienski and D. L. Esmay, *J. Org. Chem.*, **25**, 1807 (1960).

(13) F. H. Owens, R. P. Fellmann and F. F. Zimmerman, *ibid.*, **25**, 1808 (1960).

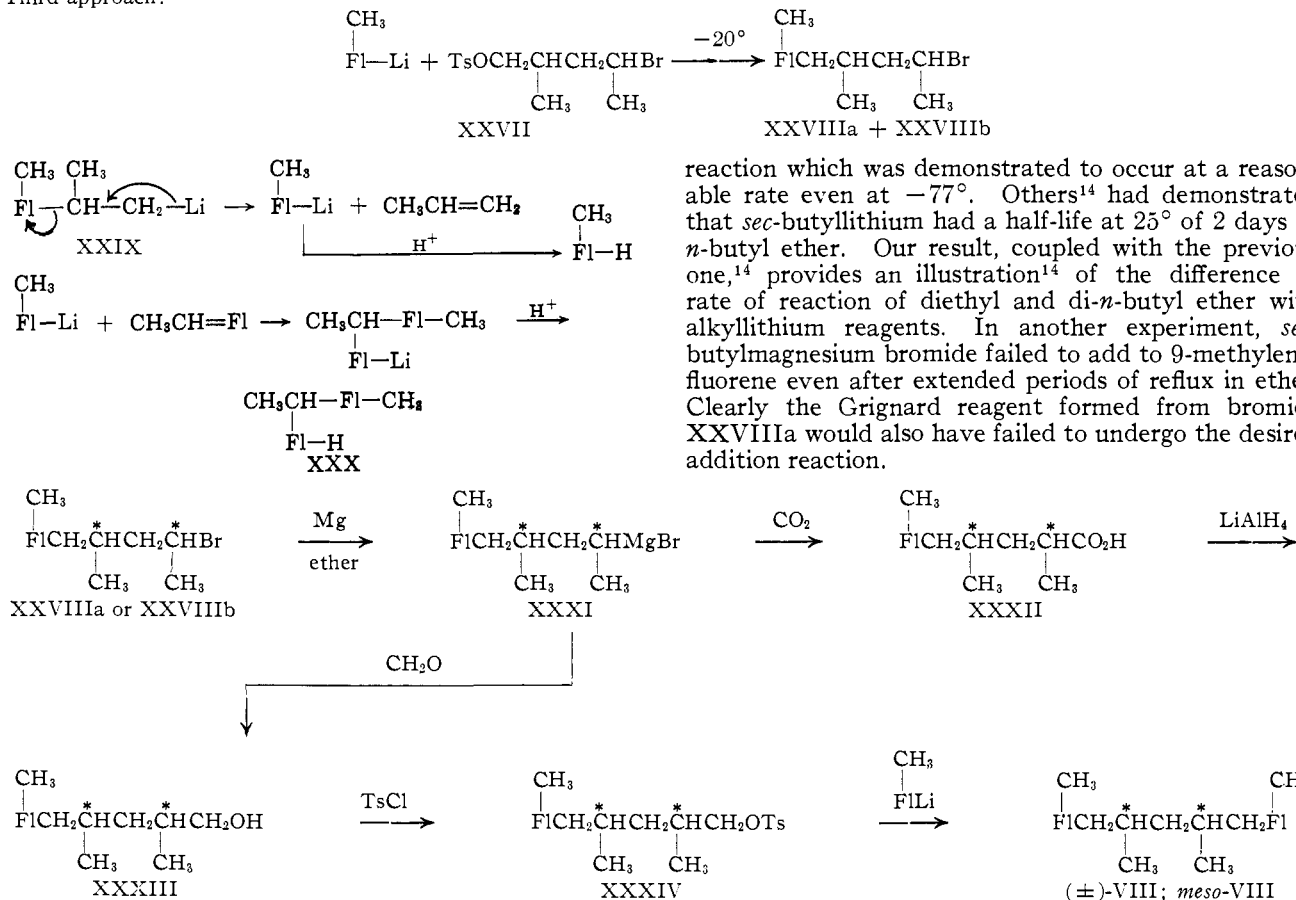
First approach:



Second approach:



Third approach:



Addition Reactions of 9-Methylenefluorene.—Previous investigators^{6b} demonstrated that although *tert*-butylmagnesium chloride adds to 9-methylenefluorene, phenylmagnesium bromide and methylmagnesium iodide do not. In the present investigation, *n*-butyllithium in ether was found to add readily to 9-methylenefluorene at -52° . However, both *sec*-butyllithium and the lithium compound prepared from bromide XXVIIa failed to add to the same olefin in ether at temperatures of -70° to 25° . As the temperature was increased, the organometallic compounds were completely protonated by the solvent, a

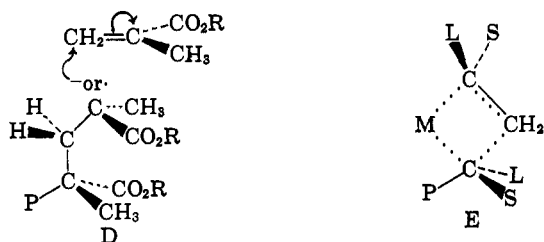
reaction which was demonstrated to occur at a reasonable rate even at -77° . Others¹⁴ had demonstrated that *sec*-butyllithium had a half-life at 25° of 2 days in *n*-butyl ether. Our result, coupled with the previous one,¹⁴ provides an illustration¹⁴ of the difference in rate of reaction of diethyl and di-*n*-butyl ether with alkyl lithium reagents. In another experiment, *sec*-butylmagnesium bromide failed to add to 9-methylenefluorene even after extended periods of reflux in ether. Clearly the Grignard reagent formed from bromide XXVIIa would also have failed to undergo the desired addition reaction.

Addition of Grignard Reagent of Bromides XXXIII to Carbon Dioxide and Formaldehyde.—Failure of the *sec*-alkyl organometallic reagents to add to 9-methylenefluorene prompted an investigation of the steric course of addition of the Grignard reagent of bromides XXVIII to carbon dioxide and formaldehyde. These two carbonyl compounds were selected because the diastereomeric products of the additions could be converted in high yields by conventional reactions (formulas) and without fractionation into hydrocar-

(14) H. Gilman, A. H. Haubein and H. Hartyfeld, *J. Org. Chem.*, **19**, 1036 (1954).

polymer chains such as B would provide fragments of opposite configurations in essentially statistical proportions.

Models for Syndiotactic Polymerization.—An open-chain model¹⁸ for syndiotactic polymerization of methacrylate esters in dimethoxyethane¹⁸ is formulated in D. Both radical and anionic initiators provide

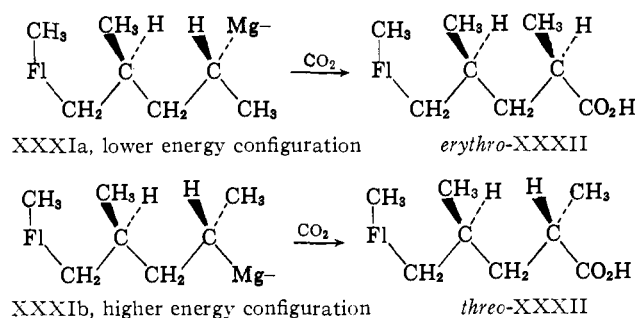


this steric result.¹⁸ That conformation for the transition state is selected which places the bulky polymer chain as far as possible from the incipient bonds. This arrangement minimizes steric interactions between the asymmetric center next to the end of the chain and the asymmetric center being formed, and minimizes dipole-dipole interactions between the carboxyl groups attached to these same asymmetric centers.

Possibly the syndiotactic 1,2-polymerization of butadiene¹⁹ involves a transition state that resembles E. In E a conformation is pictured in which the carbon-carbon bond being made occupies the least hindered position (*trans* to the bulky polymer chain). The transition state is 4-centered, and the monomer unit is arranged in such a way as to minimize repulsion between the groups attached to the two asymmetric centers that are involved. The reaction is formulated as a bimolecular electrophilic substitution at saturated carbon (SE2) with metal as leaving group and an alkene as electrophile. Examples of SE2 reactions whose stereochemistry has been examined all occur with retention of configuration,²⁰ and such a stereochemical course is formulated in E. Implicit in the formulation of E as a model for syndiotactic polymerization is the assumption that the rate of propagation exceeds the rate of epimerization of the asymmetric center which carries the metal atom at the growing end of the chain. Should this last condition not be fulfilled, stereochemical control of the course of polymerization would involve factors similar to those embodied in model D.

The failure of reaction $V + VI \rightarrow VII$ to occur prohibits an evaluation in this investigation of the hypotheses incorporated in D and E. However, the stereochemical results obtained in the addition of organometallic XXXI to carbon dioxide and formaldehyde have a bearing on some of the questions raised in formulation of these "paper models." The fact that the same steric results were obtained irrespective of which diastereomeric bromide (XXVIII) was used in preparation of the Grignard reagent indicates that equilibration of diastereomers occurred either during or after the organometallic reagent had been formed, or at both stages. Others²¹ have demonstrated that in ordinary systems, "configurational memory" is lost in converting stereomeric halides to Grignard reagents in

systems in which the halogen is attached to an asymmetric center. In the carbonation and formylation of XXXI, a small preponderance of product of *erythro* configuration was observed (*erythro*/*threo* = 1.12 to 1.27). The temperature of formation of the organometallic or of the addition reaction had little effect on the ratio of diastereomers produced (see Table I). Probably the addition reaction occurred faster than the diastereomeric Grignard reagents equilibrated, and the ratio of diastereomeric products reflects the ratio of diastereomeric Grignard starting materials. This conclusion is consistent with expectations based on conformational analysis. Although no comparison has been made of the steric requirements of magnesium of a Grignard reagent as compared to the methyl group, this latter group has been demonstrated to have greater steric requirements than the bromo-mercury group.²² Thus it is reasonable to expect that $CH_3 > Mg^-$ in effective bulk, and that configuration XXXIa is more thermodynamically stable than XXXIb.²³



These experiments serve to delineate the structural requirements for systems that might be used in future investigations of models for asymmetric polymerizations.

Experimental

2-(9-Methyl-9-fluorenyl)-propene (XI).—By known methods,⁹ 1094 g. of fluorene was converted to 1103 g. (85%) of 9-methylfluorene (IX), m.p. 45–46°. A solution of 9-lithio-9-methylfluorene was prepared by adding 9.0 g. of IX in 40 ml. of anhydrous ether to a solution of phenyllithium (prepared from 15.7 g. of bromobenzene and 1.4 g. of lithium in 100 ml. of anhydrous ether). This solution was added dropwise with stirring under dry nitrogen to a solution of 8.0 g. of acetyl chloride in 100 ml. of dry ether. The product was isolated by standard extraction and distillation procedures to give 5.4 g. of crude ketone XIII. Three recrystallizations from 95% ethanol gave 2.5 g. (32%) of white needles, m.p. 90–91° (transition of physical form, 75–76°), literature²⁴ 89°.

Methylolithium prepared from 12 g. of methyl iodide and 1.2 g. of lithium in 120 ml. of anhydrous ether was cooled to -20° , and a solution of 10 g. of ketone XIII in 50 ml. of anhydrous ether was added slowly with vigorous stirring under an inert atmosphere. The excess methylolithium was decomposed with ammonium chloride in cold water, and the *tert*-alcohol X was isolated by standard extraction and evaporation procedures. From the intensity of the carbonyl stretching frequency at 5.88μ , it was estimated that the product (11.1 g. of an oil) contained 14% of starting ketone. This oil was again treated with excess methylolithium at -20° to give product free of ketone. This product was crystallized and recrystallized from hexane to give 8.7 g. of X, m.p. 67–68° (lit.¹⁰ m.p. 68–69°).

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.75; H, 7.78.

This same alcohol X was also prepared as follows. A solution of 9-lithio-9-methylfluorene in 1.5 l. of dry ether was prepared as before from 167 g. of 9-methylfluorene and phenyllithium (from 158 g. of bromobenzene and 15 g. of lithium). A 500-ml. aliquot of this solution was cooled to -25° and 30 g. of acetone in 200 ml. of anhydrous ether was added under an inert atmosphere with vigorous stirring. The product (49 g. or 68% of X) was

(18) (a) T. G. Fox, B. S. Garrett, W. E. Goode, S. Gratch, J. F. Kinkaid, A. Apell and J. D. Stroupe, *J. Am. Chem. Soc.*, **80**, 1769 (1958); (b) J. D. Stroupe and R. E. Hughes, *ibid.*, **80**, 2341 (1958).

(19) G. Natta, *Chimica e Industria*, **42**, 1207 (1960); see also G. Natta, I. Pasquon and A. Zambelli, *J. Am. Chem. Soc.*, **84**, 1489 (1962).

(20) For example, D. Y. Curtin and W. J. Koehl, Jr., *Chem. Ind. (London)*, 262 (1960).

(21) (a) R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **99**, 45 (1911); (b) C. W. Porter, *J. Am. Chem. Soc.*, **57**, 1436 (1935); (c) A. M. Schwartz and J. R. Johnson, *ibid.*, **53**, 1063 (1931); (d) H. L. Goering and F. H. McCarron, *ibid.*, **80**, 2287 (1958).

(22) F. R. Jensen and L. H. Gale, *J. Am. Chem. Soc.*, **82**, 145 (1960).

(23) See F. A. Abd Elhafez and D. J. Cram [*ibid.*, **75**, 342 (1953)] for comparisons of thermodynamic stabilities of open-chain diastereomers.

(24) A. Meerwein, *Ann.*, **396**, 241 (1913).

isolated as before, m.p. 67–70°, undepressed by admixture with material prepared above.

Alcohol X was converted to olefin XI as follows. A mixture of 5 g. of X and 19 ml. of glacial formic acid was stirred until homogeneous, and was then warmed at 40° for 14 hr. in which time two layers formed. This mixture was stirred for 29 hr. at 26°, and poured onto a slurry of 200 g. of ice and 43 g. of 50% sodium hydroxide solution. The mixture was extracted with ether, the ether extract was washed with saturated sodium chloride solution, and the ether layer was dried and evaporated to give 4.9 g. of a pale yellow oil. This oil was chromatographed on 300 g. of neutral activated alumina. With 800 ml. of pentane, 2.3 g. (50%) of the desired olefin (XI) was eluted as a clear oil, the infrared spectra of the first and last portions of eluted material being identical. A second clear oil, 0.16 g. (10%) of 9,9-dimethyl-10-methylidenephenanthrene (XII), was eluted with 400 ml. of pentane. The infrared spectrum of the first and last fractions of this material indicated purity and a difference from XI. Elution of the column with ether gave 1.34 g. (27%) of starting alcohol X; V.P.C. of the first oil under conditions "A" (see later section) gave a single peak with retention time of 1.3 minutes, and the second oil a single peak with retention time of 2.8 minutes. The first oil was rechromatographed, and a center cut was taken for spectra and analysis, n_D^{20} 1.6083. The ultraviolet spectrum of XI in 95% ethanol gave maxima at 211, 230, 263, 291 and 302 $m\mu$ ($\log \epsilon$ 4.63, 3.88, 4.25 and 4.05, respectively). The infrared spectrum, neat, 0.022-mm. cell, gave absorptions at 3.31(m), 3.37(m), 6.12(m), 6.77(m), 6.90(s), 7.26(m), 11.24(s), 13.10(s), 13.30(s) and 13.68(s) μ . Overtones present in all other fluorene compounds from 5.0 to 5.6 μ were also present.

Anal. Calcd. for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 92.44; H, 7.18.

The 9,9-dimethyl-10-methylidenephenanthrene (XII) was rechromatographed for spectrum and analysis; n_D^{20} 1.6364. The ultraviolet spectrum in 95% ethanol showed absorptions at 213, 239, 245 and 282 $m\mu$ ($\log \epsilon$ 4.42, 4.35, 4.37 and 4.12, respectively). The infrared spectrum, neat, 0.022-mm. cell, showed strong absorptions at 3.31(m), 3.37(m), 6.15(m), 6.73(s), 6.80(m), 6.92(s), 7.25(m), 11.17(s), 13.05(s), 13.25(s) and 13.78(s) μ . The overtones in the 5.0 to 5.6 μ region were different from that of fluorene compounds.

Anal. Calcd. for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 92.60; H, 7.16.

A recycle of the residues with formic acid increased the yield to 69%. Ozonization of a sample of 0.503 g. of olefin X by the standard procedure (ethyl acetate at –32°, ozonide decomposed with zinc dust and aqueous acetic acid) gave as product 0.244 g. (49%) of ketone XII, m.p. 82–86°, undepressed by admixture with an authentic sample.

1-Bromo-2-(9-methyl-9-fluorenyl)-propane (XIV).—To a solution of 10 g. of olefin XI and 0.56 g. of benzoyl peroxide in 150 ml. of pentane was added with stirring at 25° anhydrous hydrogen bromide for 4.5 hr. When cooled to 0°, the solution deposited white crystalline product. Sodium bicarbonate powder was added until no more carbon dioxide was evolved. The reaction mixture was shaken with 300 ml. of water and 200 ml. of ether. The organic layer was washed with a solution of ferrous ammonium sulfate, water, then dried and evaporated to give 16.0 g. of white crystalline product. This material after 4 recrystallizations from hexane amounted to 10.4 g. (76%), m.p. 106–108°.

Anal. Calcd. for $C_{17}H_{17}Br$: C, 67.78; H, 5.69. Found: C, 67.78; H, 5.67.

9-Ethylidene fluorene (II).—Addition of ethylmagnesium bromide to 9-fluorenone by the usual method gave a 38% yield of 9-ethyl-9-fluorenone, m.p. 101–103°, lit.²⁸ m.p. 101°. From 54.1 g. of this alcohol was obtained by literature methods⁷ 38 g. (77%) of II, m.p. 104–105°. This compound was stored in the dark *in vacuo*.

Addition of *n*-Butyllithium to 9-Ethylidene fluorene in Hexane.—To a mixture of 150 ml. of dry hexane, 1.39 g. of a 36% mineral oil dispersion of lithium (0.8% sodium content) and crushed glass stirred under an atmosphere of dry helium was added 5.0 g. of *n*-butyl bromide. Reaction started immediately, and was complete in 3 hr. The solution was intensely blue. The reaction mixture was cooled to –15° and 1.0 g. of 9-ethylidene fluorene in 50 ml. of hexane was added slowly. No color change occurred at –15° except for splashes on the upper part of the flask. When the mixture was warmed to 5–10°, the solution turned the deep red characteristic of the 9-fluorenyl anion. The reaction mixture was stirred at 25° for 2 hr., and the excess lithium was decomposed by addition of absolute ethanol. The reaction mixture was worked up by the usual extraction procedure to give 1.7 g. of a mixture of mineral oil and 2-(9-fluorenyl)-hexane. An infrared spectrum of this material in a concentrated solution in carbon tetrachloride indicated the complete absence of olefinic or ketonic materials. The addition reaction was presumed to have gone quantitatively.

Addition of *n*-Butyllithium to 9-Ethylidene fluorene in Ether.—Extreme precautions were taken in all operations to exclude moisture and oxygen. Ether distilled from lithium aluminum hydride was employed, and all apparatus after being heated under vacuum was thoroughly washed with very dry ether. An atmosphere of dry helium was used throughout. From 0.54 g. of lithium wire (0.8% sodium) cut in a stream of pure helium and 4.22 ml. of *n*-butyl bromide (added by syringe through a serum cap) in 20 ml. of ether at –30 to –40° was prepared a clear solution of *n*-butyllithium. A solution of 4.0 g. of 9-ethylidene fluorene in 100 ml. of ether was added with stirring at –56°. The characteristic red color of the 9-fluorenyl anion appeared immediately. Product (6.0 g. of oil) was isolated in the usual way, and was shown by infrared spectra to be free of olefin. When subjected to V.P.C. analysis under conditions "B" (see later section), a single absorption peak was observed whose retention time was identical with the product obtained in hexane as solvent.

Decomposition of Organolithium Compound Prepared from Bromide XIV.—Similar products were obtained in hexane and ether, so the experiment conducted in only the latter solvent is described. The procedure employed was the same as that used in the addition of *n*-butyllithium in ether. From 10 g. of 1-bromo-2-(9-methyl-9-fluorenyl)-propane (XIV) and 0.5 g. of lithium wire (0.8% sodium) was prepared at –40° in 250 ml. of ether under helium (complete absence of moisture and oxygen) the corresponding organometallic compound. During the reaction the surface of the lithium turned a golden color. No insoluble hydroxides were present, and the reaction mixture was a clear golden color until a large amount of white precipitate separated. Addition of 250 ml. of dry, cold ether failed to dissolve the precipitate. The mixture was stirred at –25 to –35° (white precipitate and intensely orange solution) for 6 hr. The mixture was cooled to –55°, and 6.38 g. of 9-ethylidene fluorene in 200 ml. of dry ether was added with stirring. No change in color was observed. The stirred mixture was allowed to come slowly to 25°. At 15° the white precipitate and orange color persisted, but at 25° the precipitate disappeared and a clear red colored solution resulted. After remaining 30 min. at 25°, the product was isolated in the usual way, no insoluble materials being encountered.

Half the 13.5 g. of oily product was chromatographed on 250 g. of neutral activated alumina. Elution with 500 ml. of pentane gave 1.2 g. of 9-methylfluorene, identified by mixture melting point comparisons with authentic material. The next 250 ml. of pentane eluted 0.8 g. of solids which upon recrystallization from ethanol gave 0.4 g. of 9-ethylidene fluorene, identified by m.p. and mixture melting point comparisons with authentic material. An additional 2.1 g. of the same olefin was identified in the next 2 l. of pentane eluate. Elution of the column with 2 l. of 3% ether–97% pentane gave 1.5 g. of 1-(9-methyl-9-fluorenyl)-1-(9-fluorenyl)-ethane (XXX), which after two recrystallizations from ethanol gave m.p. 200–201°, undepressed upon admixture with authentic material (see below). The ultraviolet absorption spectrum in 95% ethanol gave maxima at 206, 230, 264, 291 and 302 $m\mu$ ($\log \epsilon$ 4.90, 4.24, 4.49, 4.05 and 4.20, respectively).

Anal. Calcd. for $C_{23}H_{24}$: C, 93.51; H, 6.49. Found: C, 93.58; H, 6.26.

A quarter of the original product was distilled at 0.5 mm. and a bath temperature of 21.5°. The residue, 1.13 g., was crystallized from ethanol to give 0.40 g. (11%) of XXX, m.p. 200–201°. The material in the filtrates was subjected to V.P.C. under conditions "C" (see later section) designed to detect hydrocarbons in the molecular weight range of XXX and IV. Only XXX was detected.

The remaining quarter of product was subjected to direct V.P.C. analysis under conditions "B" (see later section), with pure samples as standards. If 9-ethylidene fluorene = 100%, then 96% of this material was accounted for as: starting material, 57%; 9-fluorenone, 27%; XXX, 11%. If starting bromide XIV = 100%, then 62% was accounted for as: starting material XIV, 10%; 9-methylfluorene, 39%; compound XXX, 13%. No 9-methyl-9-isopropylfluorene was detected.

The above reaction was also run in hexane, and in ether in the presence of titanium tetrachloride with similar results. In each case, IV was demonstrated to be absent in the products.

1-(9-Methyl-9-fluorenyl)-1-(9-fluorenyl)-ethane (XXX).—A solution of 9-lithio-9-methylfluorene was prepared from 3.6 g. of 9-methylfluorene in 50 ml. of dry ether, and added to a solution of *n*-butyllithium (2.1 ml. of *n*-butyl bromide and 0.28 g. of lithium wire in 100 ml. of anhydrous ether) at –20° under dry helium. The red solution was stirred for 1 hour, allowed to come to 25°, and 1.5 g. of 9-ethylidene fluorene in 75 ml. of anhydrous ether was added dropwise with stirring. The reaction mixture was refluxed for 12 hr., the excess organolithium compound was decomposed with absolute ethanol, and the product isolated in the usual way. This material (5.6 g.) was shown by infrared comparisons to be a mixture of XXX and the two starting materials. Fractional crystallization of this mixture from ethanol gave 0.16 g. of XXX, m.p. 197–200°, undepressed by admixture

with material isolated previously. Bavin^{11a} has demonstrated that 9,9'-dimethyl-9,9'-difluorenyl can arise in solutions containing the 9-methyl-9-fluorenyl anion. This compound, which melts close to that of XXX (209–210° vs. 201–202°), depressed the melting point of XXX by many degrees when mixed with XXX.

1-(9-Methyl-9-fluorenyl)-2-propanol (XV).—A solution of 9-lithio-9-methylfluorene was prepared by addition of 90 g. of 9-methylfluorene in 200 ml. of anhydrous ether to a solution of phenyllithium (79 g. of bromobenzene and 7.0 g. of lithium) in 750 ml. of ether at 0°. The solution was stirred 15 min. and 35 g. of propylene oxide in 150 ml. of anhydrous ether was added slowly with vigorous stirring at 0°. The red color of the anion disappeared 15 min. after addition was complete. The reaction mixture was held at reflux for 5 hr., cooled to 0°, and neutralized with 500 ml. of cold 0.5 N sulfuric acid. The ether layer was washed with sodium bicarbonate solution and water. The ether solution was dried, evaporated, and the residue was distilled to give 104 g. (87%) of alcohol XV, b.p. 137–139° (0.5 mm.), m.p. 68–69°. A small portion was recrystallized 4 times from 70% ethanol; m.p. 69–71°. This material gave a positive iodoform test.

Anal. Calcd. for C₁₇H₁₈O: C, 85.67; H, 7.61. Found: C, 85.51; H, 7.37.

2-Chloro-1-(9-methyl-9-fluorenyl)-propane.—The general method of Frazer²⁶ applied to alcohol XV gave 13% of the desired chloride, m.p. 65–66° (from ethanol), and a 52% yield of 1-(9-methyl-9-fluorenyl)-propane as a clear oil, *n*_D²⁵ 1.6111 (probably *trans* isomer).

Anal. Calcd. for C₁₇H₁₇Cl: C, 79.52; H, 6.67. Found: C, 79.81; H, 6.87. Calcd. for C₁₇H₁₅: C, 92.68; H, 7.32. Found: C, 92.52; H, 7.21.

2-Bromo-1-(9-methyl-9-fluorenyl)-propane (XVI).—To a solution of 135 g. of alcohol XV in 100 ml. of dry benzene was added dropwise with stirring a mixture of 162 g. of phosphorus tribromide in 100 ml. of dry benzene. The reaction mixture was stirred at 25° for 2 hr., at reflux temperature for 10 min., then cooled and mixed with 400 g. of ice. The layers were separated, the organic layer was washed with aqueous sodium chloride solution, dried and solvent was evaporated. The residue, 180 g., was chromatographed on 500 g. of activated alumina. The first eluates (5 l. of pentane) contained 96 g. of olefin XVII, *n*_D²⁵ 1.6111, whereas later eluates with pentane contained 22 g. of crude bromide XVI, which when recrystallized three times from 95% ethanol gave 2.9 g. (2%) of pure XVI, m.p. 81.5–82.5° (needles).

Anal. Calcd. for C₁₇H₁₇Br: C, 67.78; H, 5.69. Found: C, 67.78; H, 5.74.

Further elution of the column with 5% ether–95% pentane gave 5.5 g. of crystalline 9-ethyl-10-methylphenanthrene (XVIII) which when recrystallized 3 times from 95% ethanol provided 3.6 g. (3%) of XVIII as white flakes, m.p. 85–87°, lit.²⁷ m.p. 85°; picrate m.p. 150–152°, lit.²⁷ m.p. 150°.

Addition of a large excess of hydrogen bromide gas to the above olefin XVII dissolved in anhydrous ether for 36 hr. provided an additional 34 g. of bromide XVI and an undetermined amount of XVIII. A small amount of hydroquinone inhibited peroxide-catalyzed addition.

Addition of Propylene Oxide to Grignard Reagent of Bromide XVI.—The Grignard reagent of XVI (25 g.) was formed in the usual manner. A precipitate separated during its preparation, and considerable trouble was encountered in consuming all the magnesium (2.1 g.). At 0° with vigorous stirring, 6.0 g. of propylene oxide in 125 ml. of anhydrous ether was added to the reaction mixture. After 16 hr. at reflux, the mixture was worked up by the usual method to give 24.9 g. of partially crystalline material. The oil was washed from the solid with hexane, and the crystals were recrystallized from chloroform–hexane to give 2.1 g. (12%) of 1,4-bis-(9-methyl-9-fluorenyl)-2,3-dimethylbutane (XXIa), m.p. 225–226°.

Anal. Calcd. for C₃₄H₃₄: C, 92.26; H, 7.74. Found: C, 92.29; H, 7.55.

The remainder of the product was chromatographed on 1200 g. of neutral activated alumina. Elution of the column with 3 l. of pentane gave 7.2 g. (39%) of 9-methyl-9-*n*-propylfluorene (XIX), m.p. 61–64°. Three recrystallizations of this material from 95% ethanol gave m.p. 64.5–66°.

Anal. Calcd. for C₁₇H₁₈: C, 91.84; H, 8.16. Found: C, 91.86; H, 8.29.

An additional 5 l. of pentane eluted 3.7 g. (20%) of a clear oil, presumably 3-(9-methyl-9-fluorenyl)-propene (XX). The infrared spectrum of the substance in carbon tetrachloride showed strong bands at 6.10, 7.07, 10.05 and 10.93 μ, indicative of a terminal olefin. Elution of the column with 2 l. of 5% ether–95% pentane followed by 3 l. of ether–pentane (1:1)

gave 5 g. (27%) of a second diastereomer of 1,4-bis-(9-methyl-9-fluorenyl)-2,3-dimethylbutane (XXIb). Four recrystallizations of the material from ethanol (4 times) gave pure material, m.p. 99–101°.

Anal. Calcd. for C₃₄H₃₄: C, 92.26; H, 7.74. Found: C, 92.31; H, 7.50.

With 3 l. of 5% methanol–95% ether, 3.3 g. (14%) of a crystalline material, presumably a mixture of *threo*- and *erythro*-4-methyl-5-(9-methyl-9-fluorenyl)-2-pentanol, was obtained. This material could not be fractionally crystallized into its pure components.

α-Methyl-γ-valerolactone (XXIII).—Diethyl 2-acetyl-3-methylsuccinate was prepared in 73% yield, b.p. 141–143° (14 mm.) (lit.²⁸ b.p. 145–147° (14 mm.)) by the method of Bischoff.²⁹ This compound was decarboxylated³⁰ in 73% yield to give α-methyl-γ-valerolactone (XXIII), b.p. 202–203°, lit.³⁰ b.p. 201°.

4-Hydroxy-2-methyl-1-(9-methyl-9-fluorenyl)-1-pentanone (XXIV).—A solution of 9-lithio-9-methylfluorene in 700 ml. of anhydrous ether was prepared from 79.1 g. of 9-methylfluorene, 70.7 g. of bromobenzene and 6.5 g. of lithium. This organometallic was added slowly at 0° with vigorous stirring to 50 g. of lactone XXIII in 700 ml. of anhydrous ether under dry nitrogen. After addition was complete, the reaction mixture was added to a slurry of 1500 g. of ice and 150 g. of ammonium chloride. The organic layer was washed with water, dried, and evaporated under reduced pressure to give 129 g. of a straw-colored oil. Distillation of this material at 0.25 mm. gave two fractions: 13.8 g., b.p. 140–144°; 88.3 g., b.p. 155–163°. Recrystallization of fraction 2 from hexane (4 times) gave pure 2,3-dihydro-2,4-dimethyl-5-(9-methyl-9-fluorenyl)-furan (XXV), m.p. 106–108°. The infrared spectrum of XXV showed a strong peak at 5.95 μ, typical of vinyl ethers. Tests for unsaturation were positive.

Anal. Calcd. for C₂₀H₂₀O: C, 86.92; H, 7.29. Found: C, 87.06; H, 7.25.

The remainder of fraction 2 (81.0 g.) was heated at 95° for 1 hr. with 600 g. of acetic acid, 60 g. of water and 115 g. of *p*-toluenesulfonic acid. The reaction mixture was cooled and mixed with ice and 850 g. of 50% sodium hydroxide. The resulting mixture was extracted with ether, the ether layer was washed with water, dried, and the solvent was evaporated to give 82.0 g. of 4-acetoxy-2-methyl-1-(9-methyl-9-fluorenyl)-1-pentanone (XXVI). An infrared spectrum of this material in carbon tetrachloride gave no absorption at 5.95 μ (no vinyl ether). An absorption at 5.88 μ indicated the carbonyl group had been regenerated, and absorptions at 5.68 and 8.08 μ confirmed the presence of an acetoxy group. All attempts at obtaining either diastereomer of XXVI in a pure state failed.

Attempts to reduce the carbonyl group of XXVI to a methylene group by a Wolff–Kishner reaction in diethylene glycol gave 9-methylfluorene. The standard Clemmensen reduction in acetic acid at 50° resulted in extensive elimination of acetic acid from XXVI.

4-Bromo-2-methyl-1-pentyl *p*-Toluenesulfonate (XXVII).—In 67% yield, β-methyl-δ-valerolactone was converted to ethyl δ-bromo-β-methylvalerate.³¹ The latter compound was converted to 4-bromo-2-methyl-1-pentanol as follows. To a well-stirred solution of 10.3 g. of lithium aluminum hydride at –15° was added over a period of 2 hr. 87 g. of crude ester in 450 ml. of dry ether. The mixture was stirred for an additional 15 min. at –15°, and 10 ml. of water was added dropwise. The mixture was added to ice and 500 ml. of concentrated hydrochloric acid. Sodium chloride was added, the mixture shaken, and the organic layer was washed 3 times with a 75% saturated sodium chloride solution to remove any diol produced by reduction of lactone impurity. The organic layer was dried, and solvent was evaporated to give 60 g. (97%) of 4-bromo-2-methyl-1-pentanol. This substance proved to be unstable at 25° and had to be stored at 0°. Attempts at distillation of the substance at 80° and 10 mm. resulted in decomposition to 2,5-dimethyltetrahydrofuran. The bromo alcohol was converted to its tosylate as follows.

At –20°, to a solution of 60 g. of 4-bromo-2-methyl-1-pentanol in 540 ml. of dry pyridine was added in two portions, 15 minutes apart, 95.4 g. of *p*-toluenesulfonyl chloride. The mixture was stirred for 40 minutes at –20°, and then held at 0° for 30 hr. The reaction mixture was shaken with 2 kg. of ice and 540 ml. of concd. hydrochloric acid and ether. The ether layer was washed with water, dried and solvent was evaporated under reduced pressure to yield 111 g. (100%) of tosylate XXVII as an oil. This material was stable at 25°. A small sample was dried for analysis; *n*_D²⁵ 1.5251.

Anal. Calcd. for C₁₃H₁₉BrO₂S: C, 46.57; H, 5.71. Found: C, 46.65; H, 5.69.

(28) F. Fictor and E. Rudin, *Ber.*, **37**, 1615 (1904).

(29) C. Bischoff, *Ann.*, **206**, 320 (1881).

(30) E. E. Blaise and A. Luttringer, *Bull. soc. chim.*, **33**, 820 (1905).

(31) H. N. Rydon, *J. Chem. Soc.*, 1341 (1937).

(26) M. J. Frazer, *Chem. Ind.* (London), 931 (1954).

(27) E. J. Greenhow and D. M. McNeil, *J. Chem. Soc.*, 3204 (1956).

2-Bromo-4-methyl-5-(9-methyl-9-fluorenyl)-pentane (XXVIII).—All ether in this experiment was distilled directly from lithium aluminum hydride. Under a helium atmosphere, 9-lithio-9-methylfluorene was prepared from 21.6 g. of 9-methylfluorene, 1.8 g. of lithium and 20 g. of bromobenzene in 500 ml. of ether. The resulting mixture was allowed to settle, and the clear solution was siphoned into a fresh flask under an atmosphere of helium. At -20° with vigorous stirring, this solution was added slowly to 37.5 g. of bromotosylate ester XXVII, in 300 ml. of anhydrous ether. The red color of the fluorenyl anion disappeared and a white precipitate separated. The reaction mixture was shaken with 1000 g. of ice and 150 g. of ammonium chloride, and the ether layer was washed with water, sodium bicarbonate solution, water, and was dried. The solvent was evaporated under reduced pressure to give 42 g. of an oil, whose infrared spectrum indicated only a trace of tosylate XXVII.

A small portion of the product (1.0 g.) was chromatographed on neutral activated alumina, and the major material eluted had bands in the infrared at 7.67, 10.4 and 14.42 μ absent in the original product. No evidence of terminal olefin could be detected in this product. The eluted material, probably a mixture of *cis*- and *trans*-4-methyl-5-(9-methyl-9-fluorenyl)-2-pentene, was rechromatographed and a center cut analyzed, n_D^{20} 1.5787.

Anal. Calcd. for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.60; H, 8.22.

The remainder of the product was chromatographed on 1500 g. of neutral non-activated alumina. Elution of the column with 2.5 l. of pentane gave 35.6 g. of material whose infrared spectrum showed no olefinic or tosylate absorption bands. After 2 weeks, this oil produced a sludge, which was filtered, and the solid was recrystallized from 95% ethanol to give 9.0 g. (23%) of crude diastereomer of XXVIII, m.p. 49–54°. Three recrystallizations of the substance from 95% ethanol gave m.p. 58.5–60.5°.

Anal. Calcd. for $C_{20}H_{22}Br$: C, 69.97; H, 6.75. Found: C, 69.83; H, 6.56.

The original mother liquors could not be induced to crystallize. They were dried under vacuum, and an infrared spectrum of this material (carbon tetrachloride) was essentially identical with that of the above crystalline diastereomer. A crude analysis of this oil for bromine content²⁶ indicated a minimum of 79% of XXVIII was present. This material will be referred to in later experiments as crude bromide XXVIII.

9-Methylenefluorene (VI), m.p. 51–53°, was prepared⁸ as needed from 9-chloro-9-methylfluorene³² but never isolated as such. Other methods of preparation of VI^{32,33} gave inferior yields and much polymer.

Addition of *n*-Butyllithium to 9-Methylenefluorene (VI).—This reaction was conducted under essentially identical conditions to those employed for addition of *n*-butyllithium to 9-ethylidenefluorene (see previous section). From 13.7 g. of *n*-butyl bromide and 1.39 g. of lithium wire (0.8% sodium), the organometallic reagent was formed in 125 ml. of ether at -40° under helium. At -52° , a solution of 10.0 g. of VI in 125 ml. of ether was added to the lithium reagent with vigorous stirring. An immediate red color was produced characteristic of the fluorenyl anion. The product was isolated in the usual way and distilled to give 5.1 g. of a pale yellow oil, b.p. 105–141° (1 mm.). Analysis of this material by V.P.C. under conditions "B" (see later section) showed the presence of many small peaks and one major peak at 33 minutes, slightly less than that observed for 9-(2-hexyl)-fluorene (35 minutes) under the same conditions. Clearly the major product was 9-amylluorene.

Summary of Negative Experiments.—With the same precautions applied above (helium atmosphere, completely dry conditions, lithium employed which was 0.8% in sodium), attempts were made to prepare and add 2-lithio-4-methyl-5-(9-methyl-9-fluorenyl)-pentane to 9-methylenefluorene in ether, 10 g. of the former bromide being used. The organometallic reagent was prepared at -35° to give a homogeneous solution (orange), and this was added to the olefin at -78° . No color characteristic of the 9-fluorenyl anion was produced. The product gave no peak on vapor phase analysis (condition "D") characteristic of VIII.

Under the same conditions, an attempt was made to prepare and add *sec*-butyllithium to 9-methylenefluorene in ether in the presence of 9,9-dimethylfluorene.^{11a} Carbonation of the reaction product produced only a trace of acid, which smelled like α -methylbutyric acid. No red color characteristic of the 9-fluorenyl anion was observed, and no product of addition was detected by V.P.C. analysis.

With the same precautions, *sec*-butylmagnesium bromide was prepared and treated at 0° with 9-methylenefluorene. Even at reflux temperature, no red color characteristic of the 9-fluorenyl anion was observed. When mixed with acid, much butane was evolved, and V.P.C. analysis detected no product of addition.

(32) H. Wieland and E. Krause, *Ann.*, **443**, 120 (1925).

(33) (a) H. H. Schluback and A. Fallings, *Ber.*, **85**, 514 (1952); (b) H. Wieland, F. Reindel and J. Ferrer, *ibid.*, **55**, 3313 (1922).

An attempt to form *sec*-butyllithium in ether at -78° failed. The lithium (0.8% sodium) only partially reacted. Carbonation of the reaction mixture gave 4% acidic material of bad odor, and a neutral fraction whose infrared showed three carbonyl absorptions at 5.74, 5.83 and 5.98 μ . Apparently considerable ether cleavage occurred.

Carbonation of Grignard Reagent of 2-Bromo-4-methyl-5-(9-methyl-9-fluorenyl)-pentane (XXVIII).—Runs 1–5, Table I, were all made in ether distilled from lithium aluminum hydride, in an atmosphere of helium, and employed finely divided sublimed magnesium (flake form, Dow Chemical Co.).

Run 1.—The Grignard reagent was prepared from 4.8 g. of magnesium, 17.2 g. of crude bromide XXVIII, 200 ml. of ether and 9.4 ml. of methyl iodide. The methyl Grignard reagent was first formed and then the bromide was added. After 6 hours at reflux, the mixture was cooled to -78° , and under helium poured onto an ether slurry of excess Dry Ice. The mixture was washed with 2 *N* hydrochloric acid, a dilute solution of sodium bisulfite, water, and was extracted with 500- and 250-ml. portions of 0.5 *N* sodium hydroxide solution in 70% water–30% methanol by volume. The organic layer was washed with water, dried, and the solvent was evaporated under vacuum to give 12.8 g. of non-acidic material free of hydroxyl or carbonyl absorptions in the infrared. The combined basic extracts were acidified, extracted with ether, and the ether layer was washed with water, and extracted with 250- and 300-ml. portions of 0.5 *N* sodium hydroxide in 30% methanol–70% water by volume. The combined extracts were acidified, extracted with ether, and the ether was washed with water, dried and evaporated to give 1.5 g. (10%) of a diastereomeric mixture of crystalline 2,4-dimethyl-5-(9-methyl-9-fluorenyl)-pentanoic acids (XXXII). In carbon tetrachloride, the infrared spectrum of this material exhibited a very broad hydroxyl absorption centered at 3.80 μ , and a strong carbonyl absorption at 5.89 μ .

The variations in reaction conditions for runs 2–5 are recorded in Table I. Attempts to carry out the above reaction in the absence of methylmagnesium bromide resulted in even lower yields of desired product.

Formylation of Grignard Reagent of 2-Bromo-4-methyl-5-(9-methyl-9-fluorenyl)-pentane (XXVIII).—Run 6 of Table I was conducted as was run 1 except that pure diastereomeric bromide XXVIII and formaldehyde were employed. Formaldehyde was prepared by pyrolysis of 13 g. of dry alkali-precipitated paraformaldehyde,³⁴ and was introduced into the reaction at -78° in a stream of helium. The reaction mixture was shaken with 500 ml. of 2 *N* hydrochloric acid, the ether layer was washed with dilute sodium bisulfite solution, 0.5 *N* sodium bicarbonate solution and water. The solution was dried and evaporated to an oil, whose infrared spectrum in carbon tetrachloride showed 10–15% of the oil to be the desired product, alcohols XXXIII. This estimated was based on comparisons with spectra of the alcohols prepared by lithium aluminum hydride reduction of acids XXXII.

Di-*p*-toluenesulfonate Ester of (\pm)- and *meso*-2,4-Dimethyl-1,5-pentanediol.—The *meso* isomer of 2,4-dimethyl-1,5-pentanediol (XXXV) was prepared as previously,^{15b} and the (\pm)-isomer was prepared by lithium aluminum hydride reduction of (\pm)-2,4-dimethylglutaric acid,^{15a} the procedure being patterned after that applied to similar reduction of *meso*-2,4-dimethylglutaric anhydride.^{15b} The (\pm)-diol was not characterized as such, but was used directly to prepare the tosylate.

The procedure was the same as for the preparation of 4-bromo-2-methyl-1-pentyl *p*-toluenesulfonate (XXVII) (see previous section). From 4.1 g. of *meso*-diol-XXXV and 16.4 g. of *p*-toluenesulfonyl chloride in 80 ml. of pyridine was obtained 9.7 g. of *meso*-tosylate (71%), m.p. 72–72.5° (dried *in vacuo*, m.p. 74–75.5°), crystallized from ether.

Anal. Calcd. for $C_{21}H_{28}S_2O_6$: C, 57.25; H, 6.41. Found: C, 57.27; H, 6.66.

From 1.3 g. of (\pm)-diol and 5.5 g. of *p*-toluenesulfonyl chloride and 40 ml. of dry pyridine was obtained 1.9 g. (43%) of pure (\pm)-tosylate, m.p. 103–104°. Methylene dichloride was employed as extraction solvent, and the product was purified by recrystallization from methylene dichloride–ether.

Anal. Calcd. for $C_{21}H_{28}S_2O_6$: C, 57.25; H, 6.41. Found: C, 57.00; H, 6.51.

***meso*- and (\pm)-2,4-Dimethyl-1,5-bis-(9-methyl-9-fluorenyl)-pentane (VIII).**—A solution of 9-lithio-9-methylfluorene was prepared under helium in the customary manner from 19.5 g. of 9-methylfluorene, 13.7 g. of 1-bromobutane and 1.39 g. of lithium wire in 400 ml. of dry ether at -20° . To 250 ml. of this solution was added slowly with vigorous stirring at -35° a solution of 8.8 g. of *meso*-ditosylate XXXVI in 50 ml. of anhydrous tetrahydrofuran. After addition, the reaction mixture was allowed to warm to 25°, and was stirred for 12 hr. The red color of the fluorenyl anion was still evident. The reaction mixture was shaken with

(34) J. F. Walker, "Formaldehyde," Am. Chem. Soc. Monograph Series, No. 98, Reinhold Publishing Corp., New York, N. Y., 1944, p. 24.

excess cold 1 *N* hydrochloric acid solution, and the ether layer was washed with water, dried, and the solvent was evaporated to give 13.0 g. of oil, whose infrared spectrum showed no absorption characteristic of tosylates or olefins. The oil was chromatographed on 300 g. of neutral activated alumina. Pentane eluted first 9-methylfluorene and then 7.7 g. (85%) of *meso*-VIII, m.p. 129–131°. Recrystallization of this material from ethanol gave m.p. 131–132°. A 20% solution of this material in carbon tetrachloride gave strong bands in the infrared at 3.27, 3.39, 3.43, 6.76, 6.88, 6.90, 7.26, 7.63, 8.21, 8.63, 9.72, 10.68 and 13.7 μ ; V.P.C. under condition "D" (see later section) showed a single symmetrical peak with retention time of 27.4 min.

Anal. Calcd. for $C_{35}H_{36}$: C, 92.05; H, 7.95. Found: C, 92.20; H, 7.88.

The (\pm)-isomer was prepared by the same procedure from a 100-ml. aliquot of the ether solution of organometallic reagent prepared above and 1.8 g. of ditosylate (\pm)-XXXVI. The oil obtained from the chromatograph column was recrystallized twice from 95% ethanol to give 1.2 g. (64%) of pure (\pm)-VIII, m.p. 110–111°. The infrared spectrum of the substance in carbon tetrachloride solution was essentially identical with that of its isomer; V.P.C. of the hydrocarbon under condition "D" showed a single symmetrical peak with retention time of 31.1 min. A synthetic mixture of *meso*- and (\pm)-VIII gave two completely resolved peaks in V.P.C. under conditions "D" whose retention times were 27.4 and 31.1 min.

Anal. Calcd. for $C_{35}H_{36}$: C, 92.05; H, 7.95. Found: C, 91.82; H, 8.19.

Preparation of Products of Runs 1–6 for Analyses.—Products of runs 1–5 were each reduced to XXXIII with excess lithium aluminum hydride in 50 ml. of ether in the usual way to give yields of 97–100%. These alcohols and that from run 6 were converted to their tosylates, which were free of alcohol or terminal olefin absorptions in the infrared. Yields ranged from 96–100%. Treatment of these tosylate esters with excess 9-lithio-9-methylfluorene gave hydrocarbon VIII as a mixture of diastereomers and 9-methylfluorene. Yields in this step were demonstrated to be essentially quantitative through V.P.C. comparisons with known mixtures. Solutions in carbon disulfide which were about 2% by weight in VIII were submitted to V.P.C. analysis (see next section).

After analysis of products of run 3, the material was chromatographed on 250 g. of neutral activated alumina. Elution with 1500 ml. of pentane gave 9-methylfluorene. An additional 300 ml. of pentane eluted 0.3 g. of material which by V.P.C. analysis under conditions "D" appeared to be mainly (+)-VIII. Recrystallization of this material from 95% ethanol gave 0.09 g. of (\pm)-VIII, m.p. 103–108°, undepressed by admixture with authentic compound. Elution of the column with 300 ml. of a 2% ether–98% pentane mixture gave 0.8 g. of approximately 50–50 mixture of diastereomers of VIII by V.P.C. analysis. Another 300 ml. of eluent gave 0.08 g. of material slightly rich in *meso*-VIII. Elution with 10% ether–90% pentane (300 ml.) gave material (0.3 g.) predominantly the *meso* isomer (V.P.C.

analysis). Recrystallization of the substance from 95% ethanol gave 0.10 g. of *meso*-VIII, m.p. 125–130°, undepressed by admixture with authentic *meso*-VIII. These experiments demonstrate the authenticity of the two syntheses of the diastereomers of VIII.

Analyses of Diastereomer Ratios of VIII Obtained from Products of Runs 1–6.—Conditions "D" (see next section) were used in the V.P.C. analysis. By use of a recorder with a disk-chart integrator, the area under the peaks produced by *meso*-VIII and (\pm)-VIII were measured for a 50%–50% synthetic mixture. The relative areas were constant over a large range of concentration of the original sample in carbon disulfide. However, this and other known mixtures demonstrated that the relationship between relative areas and diastereomer ratios was not constant. Hence a plot between % composition and relative peak area was made, and the ratio of diastereomers in the unknowns was determined graphically. The results are presented in Table I.

Vapor Phase Chromatography Conditions. Conditions "A."—A Perkin-Elmer model 154 vapor fractometer was used. The column was 75 cm. by 0.25 inch tubing packed with Chromosorb W upon which had been absorbed 2.5% of SE-30 silicone gum. The temperature of the column was 175° and the flow rate of helium was 80–85 ml./min. Retention times were: (2-(9-methyl-9-fluorenyl)-propene, 1.3–1.8 min.; 9,9-dimethyl-10-methylenepheneanthrene, 2.8–3.4 min.; 1-(9-methyl-9-fluorenyl)-1-propene, 1.8 min.; 1-(9-methyl-9-fluorenyl)-2-propanol, 2.6 min.; 2-chloro-1-(9-methyl-9-fluorenyl)-propane, 3.0–3.1 min.; 2-bromo-1-(9-methyl-9-fluorenyl)-propane, 3.5–4.0 min.; 9-ethyl-10-methylphenanthrene, 6.4–7.0 min.

Conditions "B."—A Loenco model 15 H gas chromatograph was used. The column was 6 ft. by 0.25 inch tubing packed with Chromosorb W upon which was absorbed 20% of SE-30 silicon gum. The preheater was at 225° and the column at 200°. The carrier gas was helium under a pressure of 12 p.s.i. Retention times were: 9,9-dimethylfluorene, 5.4 min.; 9-methylfluorene, 6.2–6.4 min.; 9-methyl-9-isopropylfluorene, 8.2–8.4 min.; 9-methylenefluorene, 9.2 min.; 9-fluorenone, 10 min.; 9-ethylidenefluorene, 16.0–17.0 min.; 9-(2-hexyl)-fluorene, 22.0 min.; 1-bromo-2-(9-methyl-9-fluorenyl)-propane, 25.6–26.4 min.

Conditions "C."—The same machine as in "B" was used. The column was 6 ft. by 0.25 inch packed with Chromosorb W upon which had been absorbed 4% of SE-30 silicone gum. The preheater was at 300° and the column at 274°. The carrier gas was helium under a pressure of 12 p.s.i. Retention times were: 1-(9-methyl-9-fluorenyl)-1-(9-fluorenyl)-ethane, 6.8 min.; *meso*-2,3-dimethyl-1,4-bis-(9-methyl-9-fluorenyl)-butane, 10.1 min.; (\pm)-2,3-dimethyl-1,4-bis-(9-methyl-9-fluorenyl)-butane, 12.0 min.

Conditions "D."—An aerograph HY-Fi model 600 chromatograph (flame detector) with a 5 ft. by 1/8 inch column packed with firebrick upon which was absorbed 5% of SE-30 silicone gum was used. The preheater was above 280° and the column was at 265°. The carrier gas was nitrogen under a pressure of 15 p.s.i. Retention times were: (\pm)-2,4-dimethyl-1,5-bis-(9-methyl-9-fluorenyl)-pentane, 31.0 min., and *meso*-2,3-dimethyl-1,5-bis-(9-methyl-9-fluorenyl)-pentane, 27.4 min.

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Studies in Stereochemistry. XXXIV. Variation of Carbonium Ion Structure with Variation in Origin¹

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The 2-phenyl-2-butyl cation has been generated in glacial acetic acid at 50° by a variety of means, and the ratios to total olefin of the *cis*- and *trans*-2-phenyl-2-butenes and of 2-phenyl-1-butene were measured. With 2-phenyl-2-butyl chloride, acetate, alcohol, amine (diazotized) and hydrazine as starting materials, the amount of *cis*-olefin varied from 70–40%; *trans*, from 1–9%; terminal, from 16–60%. The more basic the leaving group, the lower the value of the ratio, *cis*/terminal. These results demonstrate that the leaving group remains associated with the carbonium ion formed long enough to affect seriously the behavior of that ion, and suggest that the leaving group in some cases abstracts a proton from the carbonium ion. The rates at which the three olefins went to their equilibrium mixtures and the compositions of the equilibrium mixtures were determined. The assumption was made that the same carbonium ion was generated by each olefin, and the proportion of each olefin produced by the carbonium ion was calculated to be 9% *cis*, 1% *trans* and 90% terminal. Under identical conditions 2-phenyl-2-butyl acetate gave 67% *cis*, 2% *trans* and 31% terminal. These data demonstrate that conformationally different 2-phenyl-2-butyl carbonium ions lose protons more rapidly than the conformations equilibrate.

In classical carbonium ion theory, one of the arguments presented for cationic intermediates is that the same ratios of different products are observed when

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only the leaving group is changed.³ Most of the early studies involved ethanol–water solvent systems, second-

(3) (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 426; (b) K. A. Cooper, E. D. Hughes, C. K. Ingold and B. J. MacNulty, *J. Chem. Soc.*, 2038 (1948).