Solvation Control in the Anionic Polymerization of Stereospecifically Deuterated Acrylate and Methacrylate Esters

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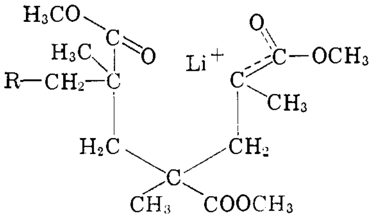
Abstract: Stereospecifically deuterated acrylate and methacrylate esters have been polymerized to highly isotactic polymers under several conditions and with a number of anionic initiators. The polymers were analyzed by nmr spectroscopy, and it was found that the proportion of *erythro-* and *threo-meso* protons within the isotactic sequence varied with monomer structure, initiator cation, and solvent composition. The presence of *erythro-* or *threo-meso* protons defines the isotactic polymerization process as occurring *via* syndiotactic-like or isotactic-like presentation of the monomer to the growing anion. The results of the simplest system, initiation by fluorenyllithium, suggest that there are two transition states leading to an isotactic placement which differ in the degree of solvation. One is derived from a "naked" contact ion pair and forms the polymer of *threo-meso* configuration. The other is apparently formed by the specifically solvated contact ion pair and forms *erythro-meso*. The solvent-separated ion pair leads to a preference for syndiotactic placement. Also, free ions, the concentration of which is negligible, are assumed to lead preferentially to syndiotactic placements.

In 1958, Fox, Garrett, Goode, and co-workers reported that the anionic polymerization of methyl methacrylate under various conditions produced crystallizable forms of stereoregular polymethyl methacrylate with three different X-ray diagrams.[2–4] The crystal lattices of polymers formed in hydrocarbon solution, in solvating media at low temperatures, and in mixtures of ethers and hydrocarbons were shown to be those of an isotactic, a syndiotactic, and a stereoblock form, respectively. The synthetic methods of the Rohm and Haas group have by now been modified and applied with similar results to a variety of acrylic and methacrylic acid derivatives,[5–7] and the mechanism of reaction has been studied in a number of laboratories.[7–23]

In summary, the picture of the anionic polymerization of methyl methacrylate in hydrocarbons that emerges from kinetic, molecular weight, and various structure studies is as follows. A rapid attack of anionic initiator on monomer occurs,[8,10,11] but in some cases the attack is indiscriminate and takes place on both olefinic and carbonyl double bonds.[10,15] A rather high mole per cent of low molecular weight by-products is thus produced initially.[10,13,15] The proportion of low molecular weight by-products including alkoxides (or their precursors) is dependent on initiator; both steric hindrance and carbanion stability increase the initiator selectivity:[7,10,23] butyllithium < fluorenyllithium < 1,1-diphenylhexyllithium.

Another substantial proportion of the growing chains is believed to become "pseudo-terminated,"[12] perhaps by forming a cyclic intermediate



which propagates only reluctantly. In addition to pseudo-terminated chains, a smaller fraction produces a propagating structure which continues to add units rapidly in isotactic placement to form a high polymer. With suitable precautions, termination can be avoided.[8,10,11] As a result of these complex processes, even though initiation is rapid and all units remain living, they do not all grow at the same rate and a wide molecular weight distribution results even in highly isotactic systems[8,13,18,23] $[\overline{M}_v/\overline{M}_n = 7\text{–}18]$. Alkoxides[9] and ethers[13] tend to compete with monomer for cation and complex reaction kinetics result. Their presence

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(1) (a) Syracuse University. (b) Bell Telephone Laboratories.

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(7) D. M. Wiles and S. Bywater, *Polymer*, **3**, 175 (1962).

(8) B. J. Cottam, D. M. Wiles, and S. Bywater, *Can. J. Chem.*, **41**, 1905 (1963).

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(10) D. M. Wiles and S. Bywater, *Trans. Faraday Soc.*, **61**, 150 (1965).

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(12) D. L. Glusker, I. Lysloff, and E. Stiles, *ibid.*, **49**, 315 (1961).

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also results in a change in stereoregularity from isotactic to stereoblock sequences,[13] in higher reaction rates,[9] and in a bimodal[9] or ultimately narrowed molecular weight distribution at high ether concentrations.

The following article is an interpretation of the mechanism of the propagation process in the anionic polymerization of acrylates and methacrylates. The minor flaws introduced by carbonyl addition and variations in molecular weight distribution will not be discussed explicitly. Our proposals will be based primarily on an analysis of nmr spectra of polymers produced from one acrylate and two methacrylate esters stereospecifically deuterated *cis* to carboxyl. Superficially it may appear that by this method one can determine whether *cis* or *trans* addition has occurred. However, *cis* or *trans* addition has no precise meaning in terms of the structure of a transition state for vinyl polymerization as it has for a four-center reaction or *cis* hydroxylation of a double bond. It has meaning only in terms of an over-all two-step process leading to a particular structure for an individual mer.

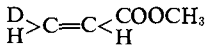
If one considers the anionic polymerization of stereospecifically β-deuterated monomers, it is clear that the direction of approach of the propagating anion to the β carbon of the monomer will determine the configuration of the β carbon introduced into the polymer. *Thus, the β configuration of a mer establishes absolutely the relative positions of the two carbalkoxyl groups in the transition state leading to its incorporation in the polymer.* Following bond formation, there is ample time for reorganization of the conformation of the propagating system by rotation around bonds. In the second bond-forming step, the monomer may, in principle, approach the new anion from either side. If it approaches from one side, the anionic mer is converted into the same α configuration as its predecessor; if from the other it is converted to the opposite α configuration. If the unit adopts the same α configuration as its predecessor, we can determine the initial mode of approach at the β carbon from the methylene nmr spectrum, but if it adopts the opposite configuration, the information regarding the preceding transition state is lost since the methylene positions are placed in identical magnetic environments. *Thus, tacticity at the α and β positions establishes absolutely the direction of bond formation at the respective centers.* Many different models of transition states may still be consistent with the information obtained, but they must fit the requirements of the direction of bond formation at both centers and the relative positions of the two carbalkoxyl groups during bond formation. In addition, any model for isotactic polymerization should explain the repeated isotactic placements which are not expected to occur from consideration of nonbonded interactions between terminal and penultimate mers.

For a complete interpretation of the mechanism, it is necessary to know not only the structure of monomer and polymer, but also the nature of the active propagating species. In anionic systems, many different kinds of species are possible having different degrees of solvation, ionization, and association, and for several anionic systems we will present only the general features of the polymerization. However, a considerable body of knowledge exists regarding the structure of lithium alkyls, arenyls, and polystyryls in a number of solvent systems. Reasonable analogies can, therefore, be applied to the anionic polymerization of the acrylates and methacrylates with lithium counterion, and we will propose that certain specific ionic species retain their identity and general conformation during several monomer additions and that these can, therefore, be considered propagation sites in the sense used by Coleman and Fox.[24]

In our initial work,[25] isopropyl acrylate was polymerized in toluene with phenylmagnesium bromide as initiator at −78°. Model polymerizations of the undeuterated monomer gave an nmr spectrum that almost exactly matched a calculated spectrum for the corresponding cyclic isotactic dimer with α proton at τ 7.43 and β protons at 7.86 and 8.32, using a six-spin model. The racemic protons, identified in free-radical polymerized product, are centered at τ 8.16, and these were absent so the system produced essentially pure isotactic polymer. When isopropyl α-*cis*-β-d_2-acrylate was polymerized under identical conditions, an isotactic polymer was produced with *meso* proton peaks at both τ 7.86 and 8.32 and in nearly equivalent amounts. Thus, roughly equal amounts of isotactic-like and syndiotactic-like approach to β methylene had occurred, although the α configuration of the polymer was highly isotactic.

The *erythro* and *threo* configurations in this polymer could have been distributed along the chains in random, syndiotactic, or stereoblock sequences, of which only the first two alternatives were initially considered by us.

At the same time that our first communication appeared, a very similar study by Yoshino and co-workers showed that anionic polymerization of deuterated methyl acrylate by $LiAlH_4$ led to a single definite mode of opening[26] which he later established as *trans* (*threo–meso* or isotactic-like approach).[27] Shortly thereafter, results of experiments (suggested by the work of Yoshino) obtained in this laboratory demonstrated that the mode of approach of anion to monomer was very sensitive not only to the initiator used but also to any added solvent such as ether. Qualitatively, then, it appears that conditions which alter the configurations of the α-carbon atom from isotactic to stereoblock sequences also alter the direction of approach of anion to monomer and the configuration of the β-carbon atom. Furthermore, the β-carbon atom configuration is more sensitive to changes in reaction conditions than the α configuration. It is, therefore probable, by analogy to the stereoblock distribution of α configurations, that β *erythro*– and *threo–meso* configurations may also occur in blocks. Yoshino[28] has devised an ingenious experimental test to distinguish among the three possible distributions of β configurations using the coupling patterns of an isotactic polymer synthesized by Grignard initiation of



$$\overset{D}{\underset{H}{}}\!>C=C<\!\overset{COOCH_3}{\underset{H}{}}$$

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(27) T. Yoshino, M. Shinomiya, and J. Komiyama, *ibid.*, **87**, 387 (1965).

(28) T. Yoshino and K. Kuno, *ibid.*, **87**, 4404 (1965).

Table I. Viscosity of Polymer Solutions in Toluene Immediately before and after Termination

Polymer no.	Temp, °C	Efflux time, sec			$\eta_{sp} = (t - t_0)t_0$		η_{sp}(live)/ η_{sp}(dead)
		Solvent, t_0	Living	Terminated	Living	Terminated	
d	−75	113	1740	1485	14.4	12.1	1.18
e	+19	93	152	163	0.64	0.75	0.85
f	−75	113	917	952	7.1	7.4	0.96

Table II. Conductivity Measurements of 1,1-Diphenylhexyllithium and 1,1-Diphenylhexyllithium-Initiated Poly(ethyl methacrylate-d_1) in Toluene and in THF at −78°

Species	Solvent	Concn × 10^2, *M*	*R*, ohms	mho cm^2/equiv[a]		α	K_d[b]
				Λ	Λ_0		
Initiator e	PhMe	0.50	*d*				
Living polymer e	PhMe	0.36[c]	*d*				
Initiator j	THF	1.5	2150	0.7	18	3.9×10^{-2}	2.28×10^{-5}[e]
Living polymer j	THF	1.42[c]	1.35×10^5	1.18×10^{-2}	10	1.18×10^{-3}	2×10^{-8}

[a] Λ_0 was estimated using the data in ref 31b or by comparison to polystyrene systems. An error in λ_0^- for the polymer anion by a factor of even two will not seriously affect the K_d for the polymer. [b] $K_d = \alpha^2 c$, where $\alpha = \Lambda/\Lambda_0$. [c] 100% initiation was assumed; the lower molarity is due to the dilution of the initiator solution by the monomer and solvent. [d] Resistance was too high to measure. [e] This value is in good agreement with the previously reported value for fluorenyllithium[31b] ($K_d = 1.99 \times 10^{-5}$) at −70°.

In the case of this catalyst system at least, and probably in others, it appears that stereoblock sequences of *erythro*- and *threo–meso* configurations are formed, and, although the present work does not specifically establish that point, our mechanism for polymerization with Li counterion implies the same phenomenon.

Results and Discussion

The most profound differences in α and β tacticity between polymers produced under different conditions can be related to the counterion, the ratio of Lewis base (diethyl ether or tetrahydrofuran) to initiator, and the temperature during polymerization. Since our most complete results are those relating to propagation with lithium counterion, these will be discussed first.

Organolithium compounds can exist in the following forms: (1) molecular complexes, *i.e.*, dimers, hexamers, etc.; (2) contact ion pairs, not specifically solvated; (3) contact ion pairs, peripherally solvated; (4) solvent-separated ion pairs; (5) dissociated ions and ion multiplets such as triple ions. These five groups are listed in order of increasing solvation, which is favored by solvents of high dielectric constant. Ion association and molecular complexes are favored at high concentrations, the latter in hydrocarbon solvents.

In order to test for the presence of molecular complexes in our systems, we have shown that a solution of "living" polyethyl methacrylate with lithium counterion in toluene has the same viscosity before and after killing with agents having an active hydrogen (Table I). Since destruction of molecular complexes would occur on this treatment, there must be none present in toluene and their presence, therefore, need not be considered in toluene or, of course, in toluene–ether mixtures. In contrast, similar viscosity experiments with isoprene by Morton[29] and kinetic studies with living polystyrene by Bywater[30] have shown the presence of molecular complexes in those polymerizations. Since the propagating lithium$^+$–acrylate$^-$ ion pair is in a domain of polymeric ester functions, its failure to associate with other polymeric anions or ion pairs is not surprising.

The lithium–poly(ethyl methacrylate) system in pure tetrahydrofuran, even at −78°, shows a trivial conductivity which establishes the essential absence of dissociated ions[31a] (Table II). Increasing temperatures or increasing amounts of hydrocarbon would decrease dissociation; therefore, in all hydrocarbon–tetrahydrofuran systems dissociated ions can be ignored. These results are consistent with recent work on lithium fluorenyl by Hogen-Esch and Smid of this laboratory,[31a] and are further supported by common ion effects discussed later.

We will, therefore, propose that differences in the configuration of polymers produced under different experimental conditions reflect differences in the proportion of three propagating species: unsolvated contact ion pairs, peripherally solvated contact ion pairs, and solvent-separated ion pairs. These will be present in largest proportion in hydrocarbon systems, hydrocarbon systems with small amounts of ether, and ether-rich systems, respectively.

In our experiments, changes in monomer concentration (0.02–1 *M*) and monomer to initiator mole ratios (7–250) seemed to exert little or no influence on tacticity at α (*cf.* ref 10 and 13) or β position (*cf.* Tables III and IV). Differences in tacticity between molecular weight fractions were also minor, for the petroleum ether soluble portions of the polymers investigated are only slightly less isotactic than the petroleum ether insoluble portions (*cf.* ref 13) and the changes in *erythro–meso* with changes in the base/initiator ratio are parallel in the two fractions (*cf.* Tables III and IV). The anionic center is propagating within a polymeric ester domain which is little changed by differences in these parameters.

Anionic polymerization of all three monomers in the presence of the lithium cation and in the absence or near absence of ether produces *threo–meso* polymer preferentially. This is the structure that would be produced by an isotactic-like approach of anion to monomer (see Figure 1). Since under these conditions the predominant or only species present is an unsolvated contact ion pair, this must be responsible for the formation of the *threo–meso* structure. Typical ex-

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(29) M. Morton and L. J. Fetters, *J. Polymer Sci.*, **A2**, 3311 (1964).
(30) S. Bywater and D. J. Worsfold, *Can. J. Chem.*, **40**, 1564 (1962).
(31) (a) T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, **88**, 307 (1966); (b) *ibid.*, **88** 318 (1966).

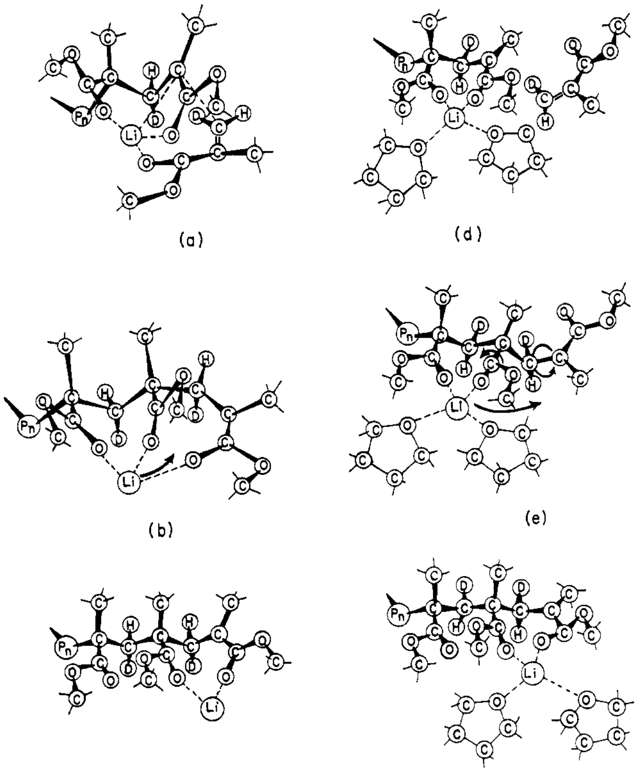
periments demonstrating this relationship are found in Table III (compare polymers a, d, e, f, g to those produced from the same monomer at higher $(\mathrm{THF})/(\mathrm{I}_0)$ ratios).

If a single species is responsible for the propagation of all polymers in a particular system, the polymer should obey the single σ relationship of Bovey and Tiers[16] or one of the Markov models. The polymers prepared in the presence of very little or no ether appear to approach the former (Bernoullian) relationship as do the polymers prepared by Bywater[10] in ether-free solution initiated by 1,1-diphenylhexyllithium (but not by butyllithium). The number-average length of sequences of *meso* placements, $\mu(m)$,[32] in these polymers is rather long and interrupted only occasionally by a racemic placement which appears in a heterotactic triad. The structure of the polymer thus appears to be primarily of isotactic blocks in which the ester functions in alternating sequences lie on opposite sides of the polymer chain in zigzag conformation. Such a structure could be produced by an occasional rapid inversion of the propagating site.

The analysis of the fluorenyl- and 1,1-diphenylhexyllithium initiated polymerization of ethyl methacrylate at $-78°$ in pure tetrahydrofuran also appears reasonably straightforward. The largely syndiotactic polymer produced apparently satisfies the single σ relationship (polymers j, k, l) and can, therefore, justifiably be assumed to be produced at a single kind of propagation site. Since the living polymer shows a trivial conductivity, as stated above, the propagating site is assumed to be a solvent-separated ion pair. This conclusion is also consistent with the fact that when the polymerization was repeated with sufficient lithium tetraphenylboron to decrease the concentration of any dissociated ion by a factor of 150, there was little observable difference in nmr spectra of the two polymers (polymers k, l). If both species are present, each must produce racemic placements. Although the sequence length of racemic placements is on the average much longer than that of *meso* placements, the *meso* units are not isolated, and the structure as defined by these parameters also is consistent with a single probability of placement.

It now remains to describe the polymerization with lithium counterion in mixed hydrocarbon–ether solvents. The simplest example of such a polymerization is that of ethyl methacrylate at $+30°$ (polymer h, Table III). In contrast to the ether-free systems, nearly all *meso* placements result from the opposite approach—syndiotactic-like—as shown by the low ratio of $(tm)/(m)$. The sequence lengths of *meso* and racemic placements as well as the triad structure indicate that this polymer is still isotactic, though slightly less so than the others, *even though the mechanism of addition is different.* Since the propagating species is presumably intermediate in solvation between a "naked" contact ion pair and a solvent-separated ion pair, we have proposed that it is peripherally solvated.

When the polymerization is run under identical conditions except at a low temperature, $-78°$, the system propagates a stereoblock polymer (polymer i). The proportion of *meso* diads and isotactic triads decreases markedly and a higher proportion of syndiotactic placements is generated in longer sequences. It is clear that by lowering the temperature in this system some of the peripherally solvated contact ion pairs have been converted to solvent-separated ion pairs, that both species propagate polymer, one with a substantial preference for the formation of *erythro-meso* structures, the second with a preference for racemic. It is of interest that the *meso* sequence length is nearly unchanged with temperature, and the racemic sequence length increases.



(c) Threo meso (f) Erythro meso

Figure 1. (a) An isotactic-like approach of the monomer to the chelated contact ion pair. (b) The new C–C bond has been formed with the methylene D on the same side of the zigzag as the ester function. (c) The Li^+ moves up to the new anion, with concurrent rotation of the new penultimate ester group, forming the same chelated structure as in a. (d) A syndiotactic-like approach of the monomer to the peripherally solvated contact ion pair. There is no coordination of the monomer carbonyl with the counterion, and nonbonded interactions force the approach into syndiotactic like. (e) The new C–C bond has been formed. (f) The Li^+ and its peripheral solvent shell moves up to the terminal unit, with concurrent rotation of the ester function. As the new anion resides largely on the carbonyl, there is a simultaneous rotation about the new α,β bond to reduce charge separation. This results in an *erythro-meso* placement, the methylene D being on the opposite side of the zigzag from the ester groups and the α carbon now in an incipient isotactic configuration.

The interpretations given above are consistent with the trends obtained on all three monomers. However, whenever two monomers were polymerized under nearly identical conditions, the one with the larger ester function produced the higher proportion of *erythro-meso* structures [lower $(tm)/(m)$ ratio] (polymers m *vs.* i and g *vs.* a). This result suggests that bulkier ester functions favor a syndiotactic-like approach.[33]

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(32) By definition $\mu(m)$ and $\mu(r)$ are physical constants which are valid irrespective of reaction mechanism.

(33) L. L. Ferstandig and F. C. Goodrich, *J. Polymer Sci.*, **43**, 373 (1960).

Table III. Polymerization in Toluene, in Tetrahydrofuran, and in Mixtures with Lithium Counterion

Conditions	Number												
	a	b	c	d	e	f	g	h	i	j	k	l	m
Monomer	*i*-PrA	*i*-PrA	*i*-PrA	EMA	EMA	EMA	EMA	EMA	EMA	EMA	EMA	EMA	MMA
Initiator	Fl–Li	Fl–Li	Fl–Li	Fl–Li	DPHL	BuLi	Fl–Li	Fl–Li	Fl–Li	DPHL	Fl–Li	Fl–Li	Fl–Li
$(ROR)/(I)_0$	2.5	16	32	0	0	0	2.5	7.5	7.5	850	22,000	33,000	6
$(M)_0/(I)_0$	200	42	62	154	36	18.5	250	20	20	6.5	45	67	62
Solvent	PhMe	PhMe	PhMe	PhMe	PhMe	PhMe	PhMe	PhMe	PhMe	THF	THF	THF	PhMe
Ether	THF	THF	THF	...	...	...	THF	THF	THF	THF	THF	THF	THF
$(M)_0$, *M*	0.14	0.89	0.96	0.114	0.13	0.114	0.056	0.93	0.93	0.094	0.025	0.024	0.98
$(I)_0$, *M*	0.0007	0.021	0.015	0.00074	0.0036	0.0062	0.00023	0.047	0.047	0.014	0.00055	0.00036	0.016
(Ether), *M*	0.0018	0.33	0.49	...	...	...	0.00057	0.35	0.35	12	12	12	0.095
$(Li(Ph)_4B)$, *M*												0.0023	
Temp, °C	−78	−78	−78	−78	−78	−78	−78	+30	−78	−78	−78	−78	−78
					Nmr, petroleum ether insoluble								
(*m*)	86	83	82	87	94	96	91	80	64	27	15	18	79
(*tm*)/(*m*)	45	24	11	88	85	83	83	9	11	42	51	42	66
(*i*)				79	89	91	85	72	55	7	5	6	70
(*h*)				16	10	8	12	17	18	40	21	26	19
(*s*)				4	1	1	3	11	27	53	74	68	11
$\mu(m)$				10.5	18.4	23.0	14.6	9.6	7.2	1.3	1.5	1.4	8.4
$\mu(r)$				1.5	1.1	1.0	1.4	2.3	4.0	3.7	7.9	6.2	2.2
					Nmr, petroleum ether soluble								
(*m*)	77	88	72	89	90	85		78	84			21	
(*tm*)/(*m*)	45	27	14	75	67	68		9	12			31	
(*i*)				80	83	74		64	73			2	
(*h*)				18	14	22		27	23			38	
(*s*)				2	3	4		7	4			60	
$\mu(m)$				10.2	12.7	7.8		5.5	7.2			1.1	
$\mu(r)$				1.2	1.4	1.4		1.5	1.3			4.2	

Table IV. Polymerizations Using Counterions Other Than Lithium

	Number							
Conditions	n	o	p	q	r	s	t	u
Monomer	EMA	*i*-PrA	*i*-PrA	*i*-PrA	*i*-PrA	*i*-PrA	EMA	MMA
Initiator	Fl–Cs	$LiAlH_4$	PhMgBr	PhMgBr	PhMgBr	PhMgBr	PhMgBr	PhMgBr
$(ROR)/(I)_0$	520	10	0.05	2	0.5	9	9	9
$(M)_0/(I)_0$	36	100	74	12.5	25	25	25	25
Solvent	THF	PhMe	PhMe	PhMe	PhMe	PhMe	PhMe	PhMe
Ether	THF	Et_2O	Et_2O	Et_2O	Et_2O	Et_2O	Et_2O	Et_2O
$(M)_0$, M	0.75	1.0	0.96	0.97	0.87	1.0	1.0	0.96
$(I)_0$, M	0.021	0.01	0.013	0.078	0.035	0.04	0.04	0.038
(Ether), M	11	0.1	0.0007	?	0.018	0.36	0.36	0.35
Temp, °C	−78	−78	−78	−78	−78	−78	−78	−78
Nmr, petroleum ether insoluble								
(m)	28	84	95	100	85	82	96	45
$(tm)/(m)$	70	86	29	50	59	95	96	79
(i)	5						94	32
(h)	47						4	27
(s)	48						2	41
$\mu(m)$	1.2						48	3.3
$\mu(r)$	3.0						1.8	4.0
Nmr, petroleum ether soluble								
(m)	42	84	72		79	73	93	
$(tm)/(m)$	53	81	50		65	88	94	
(i)	17						90	
(h)	49						6	
(s)	33						4	
$\mu(m)$	1.7						31	
$\mu(r)$	2.3						2.4	

The behavior of the three postulated intermediates can be rationalized by the mechanism in Figure 1.

In the absence of ether the propagating anion can be pictured as being present in a contact ion pair in which the Li ion is chelated with the terminal and penultimate carbonyl functions. Even if the terminal unit is in the enolate form, retention of configuration during reaction could be expected because of the contact ion pair. The monomer coordinates with the lithium ion before reacting with the anion and thus adopts an isotactic orientation before the covalent bond is produced between the anion and monomer. When bond formation occurs, *threo* configuration results, and the configuration of the anion is retained in the new contact ion pair until the next propagation step.

When a little ether is present, it competes successfully with the less basic monomer for the coordination shell of the metal ion but does not displace the chelated structure. The monomer, therefore, does not coordinate before reaction but approaches the anion in the syndiotactic sense which is sterically preferred because of the usual nonbonded interactions[33] and those with the solvent shell. After reaction, rotation around the α,β bond permits the new terminal anion to be coordinated with the metal ion and its configuration retained until the next propagation step within the solvated (and chelated) contact ion pair. Since chelation is preferred, it is not surprising that the peripherally solvated contact ion pair should preferentially produce *meso* placements *via* syndiotactic-like approach. It is also not surprising that some racemic placements should also occur before reorganization and formation of a new chelate.

It is to be expected that in solvent-separated ion pairs the chelate ring will be broken; the penultimate and terminal units will adopt a syndiotactic conformation.[34] The monomer will also probably approach the anion in a syndiotactic sense,[33,34] just as with dissociated ions. Polymerization will thus proceed as from a freely propagating species, the single σ relationship will hold, and syndiotactic placements will be preferred.

The interpretation we have made above of the polymerizations with the lithium counterion is consistent with a variety of previous observations. It is well known that coordination of metal ions with electron donors is favored by small atomic size. It is also known that in ether-free systems, higher isotacticity is obtained with lithium than with sodium or potassium.[14,19] In ether-free systems, coordination with the monomer will also be favored by low temperatures, and this fact as well as an entropy factor probably accounts for slightly increased isotacticity sometimes observed at low temperatures in anionic systems.[2,3,5a]

In ethers, the order of solvent-separated ion pair formation is Li > Na > K,[31a] and the same order of production of syndiotactic placements has been observed.[19–21] Although a very small fraction of highly reactive dissociated ions might produce all the syndiotactic polymer, this does not seem likely since with styrene, the solvent-separated ion pair approaches the free ion in reactivity.[31a] In contrast to hydrocarbon systems, anionic initiators in the presence of ethers produce fewer isotactic placements at lower than at higher temperatures,[14,17,19,20] as expected from the higher proportion of solvent-separated ion pairs.[31a] For the same reason ethers of higher basicity result in the formation of less isotactic polymers in the polymerization of methacrylates in toluene with Li counterion.[14]

Glusker has investigated kinetically the polymerization of methyl methacrylate in toluene–tetrahydrofuran mixtures.[13] Although his assumptions do not entirely fit our mechanism, he concludes that isotactic polym-

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(34) J. W. L. Fordham, *J. Polymer Sci.*, **39**, 321 (1959).

erization is permitted even when at least one tetrahydrofuran molecule is associated with each growing chain and that this species alters the kinetics of the reaction. In the region of tetrahydrofuran concentration where the propagation is predominantly syndiotactic, he finds that four tetrahydrofuran molecules are associated with each living chain.

The mechanistic model proposed here uses the concept of a chelated structure to explain repeated α-isotactic placements. The same assumption has been made previously by Cram,[35] Goode,[15] and Bawn and Ledwith.[36] The prior models, however, do not permit an explanation of the variable tacticity observed on the β carbon by us and by Yoshino and co-workers. This model does fit closely the multiple site concept proposed by Coleman and Fox.[24] Further analysis of this aspect of the work will be presented later.

Fluorenylcesium, in contrast to fluorenyllithium, exists in tetrahydrofuran primarily as a contact ion pair,[31a] and it appears probable that the propagating anion–cesium cation complex has a similar structure. Furthermore, the cesium cation has little tendency to coordinate with or become solvated by nucleophiles.[31a,37] It is, therefore, not surprising that poly(ethyl methacrylate) (polymer n, Table IV) produced with the cesium counterion in tetrahydrofuran is quite different from that produced with lithium. The polymer contains a few more *meso* methylenes but almost no isotactic triads. A polymer structure consisting almost exclusively of heterotactic and syndiotactic triads has, to our knowledge, not been observed previously. Various mechanisms can be proposed for its origin but, in the absence of further data, we will not suggest any at this time.

The Grignard initiation system (Table IV) is more complex than those described above and has some similarities to and some differences from lithium initiation. Again, the low and high molecular weight fractions are of similar tacticity on both the α and β positions. Again, the addition of ether to the polymerization system alters the proportions of *threo–* and *erythro–meso* configurations in the polymer. However, in this system *erythro–meso* is preferred at low ether concentrations and *threo–meso* at higher ether concentrations. Finally in the Grignard system, the tacticity of methyl methacrylate is far more sensitive to the presence of ether than is either ethyl methacrylate or isopropyl acrylate. This is shown in both the methylene and α-methyl regions of the spectrum and is consistent with many older observations in related systems that branched or bulky functional groups assist in formation of isotactic polymers. The poly(methyl methacrylate) produced in the presence of small amounts of ether is, as has also been shown before, a stereoblock structure and does not follow the single σ relationship.

It is probably premature to describe a transition state for phenylmagnesium bromide or lithium aluminum hydride initiated polymerizations. Various speculations are described elsewhere.[38]

It is obvious that without β-deuterated monomers, the mode of monomer approach would not be possible to ascertain. However, this is not the only advantage of deuterated monomers. In the isopropyl α-β-d_2-acrylate, the *meso* and racemic peaks are clearly defined; this is not possible in the nondeuterated monomer owing to vicinal coupling with the α proton. Furthermore, the spectra of both the acrylates and methacrylates are greatly simplified by the elimination of the methylene geminal coupling. This simplification makes it possible to see tetrad structures.[39–41] As now we are looking at sequences in the chain that are four units in length, considerable insight into the micro structure and the propagation mechanism may be gained. Furthermore, tetrads allow for the first time statistical models such as first-order markovian to be tested.[39] This work is now in progress and will be reported in the near future.

Experimental Section

Materials. Isopropyl propiolate was prepared using a procedure similar to that of Noller.[42] The yields ranged from 32 to 55%.

Isopropyl α-*cis*-β-d_2-acrylate was prepared in a high vacuum system using a vacuum modification of a synthesis by Castro, *et al.*[43] Isopropyl propiolate (10 ml, 84 mmoles, degassed) was distilled into a solution of chromous chloride (25 g, 203 mmoles) in degassed deuterium oxide (100 g, 99.5%), and the mixture was stirred overnight. The volatiles were stripped off and extracted with petroleum ether. Vapor phase chromatography analysis indicated complete reaction of the acetylenic material, with about 1–3% complete reduction to the saturated compound. After concentrating the solution by flash distillation at 300 torr, the pure acrylate ester was isolated using preparative vpc (Wilkens Autoprep, Carbowax 20M column). A typical yield was 2.9 g or 30%. Nmr analysis of the ester[25] indicated 100% *trans* labeling.

Methanol-*d* and ethanol-*d* were prepared using the procedure of Streitwieser;[44] these were checked for isotopic purity with nmr spectroscopy.

Ethyl *cis*-β-d_1-methacrylate was prepared using the method of Jones[45] except that a cold finger condenser was used to retain methylacetylene in the reaction vessel. A mixture of nickel carbonyl (16 ml, 0.12 mole) and ethanol-*d* (50 ml) was allowed to drip into a mixture of ethanol-*d* (100 ml) and deuterium chloride (20 ml, 12 *N* in D_2O) through which methylacetylene was being bubbled. After the reaction and work-up was completed, pure monomer was isolated as needed using a preparative vpc. The yield was estimated by vpc to be 18.5 g, 26% of theoretical.

Nmr analysis of the monomer showed the following: τ 3.96, a complex peak with relative area 0.1; τ 4.54, a quartet with relative area 1, J = 1.5 cps; τ 8.1, doublet, relative area 3, J = 1.5 cps; τ 5.85, quartet, relative area 2, J = 7.2 cps; τ 8.71, triplet, relative area 3, J = 7.2 cps. These were given the following assignments: β-*cis* proton, β-*trans* proton, α-methyl, ester methylene, and ester methyl, respectively. The β-*cis* proton is an impurity, and is present to the extent of 10%. An expansion of the complex peak revealed at least six peaks; this plus the ratio of peaks indicates that the impurity is undeuterated ester and not the *trans*-deuterio isomer.

Methyl *cis*-β-d_1-methacrylate was prepared in an analogous manner, obtaining a yield of 2.6 g or 5%. The low yield is thought to be due to the limited solubility of the nickel carbonyl in methanol-*d*. Nmr analysis showed a complex multiplet at τ 3.98, assigned to the β-*cis* proton; a quartet at τ 4.54, J = 1.5 cps, assigned to the β-*trans* proton; a doublet at τ 8.12, J = 1.5 cps, the α methyl;

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(35) D. J. Cram, *J. Chem. Educ.*, **37**, 317 (1960).

(36) C. E. H. Bawn and A. Ledwith, *Quart. Rev.* (London), **16**, 361 (1962).

(37) C. Carvajal, K. J. Tolle, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, **87**, 5548 (1965).

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(43) C. E. Castro and R. D. Stephens, *ibid.*, **86**, 4358 (1964).

(44) A. Streitwieser, Jr., L. Verbit, and P. Stang, *J. Org. Chem.*, **29**, 3706 (1964).

(45) E. R. Jones, T. T. Shen, and M. C. Whiting, *J. Chem. Soc.*, 230 (1959).

and a singlet at τ 6.32, the ester methyl. For the same reasons mentioned above, the 10% impurity is believed to be the undeuterated ester.

Phenylmagnesium bromide was made and stored in the conventional manner under nitrogen. Withdrawals were made with a dried and nitrogen-flushed hypodermic syringe. The solution was standardized by titration and was 1 *N*.

Lithium aluminum hydride powder was stirred with anhydrous ether and filtered. The solution was handled in the same manner as the Grignard solution, and was standardized by measuring gas evolution from water–dioxane.

Fluorenyllithium and -cesium were prepared by dissolving fluorene, which had been recrystallized two or three times from ethanol, in purified and dried tetrahydrofuran[31a] and then stirring the solution over the metal.[46] The yellow or red solution was filtered through a fritted glass filter into breakseals and sealed off. The entire operation was carried out under high vacuum (less than 10^{-5} torr) under rigid oxygen- and moisture-free conditions in an all-glass system previously washed with the anion solution. The concentrations of the solutions were determined optically using a 0.0094-cm, quartz, high-vacuum cell in a Cary Model 11 spectrophotometer; the molar extinction coefficients are given elsewhere.[31a] The concentration of the fluorenyllithium was 0.08 *M* and of the fluorenylcesium, 0.03 *M*.

The ethereates of fluorenyllithium and the Grignard were prepared in toluene by distilling away the excess ether from the respective solutions on a high-vacuum line, then distilling in toluene which had been stirred over three fresh batches of CaH_2 on the high-vacuum manifold with degassing. The toluene was then distilled off the salt, and the salt was pumped out at elevated temperatures: 100° in the case of the Grignard and 85° in the case of the fluorenyllithium. This rinsing procedure was repeated, then a final portion of toluene was distilled in and the solution was filtered through a fritted glass filter into an ampoule and sealed off.

Ether-free fluorenyllithium in toluene was prepared under high vacuum by the exchange between ethyllithium and fluorene. A benzene solution of ethyllithium (4 ml, 0.5 *N*, 2 mmoles, repeatedly recrystallized from benzene) and fluorene (664 mg, 4 mmoles) was released from breakseals into a reaction vessel previously washed by lithium alkyl. The solution was stirred at 50° for 1.5 hr, then at ambient temperature overnight. The yellow solution was filtered through a fritted glass filter into breakseals and sealed off, leaving on the filter an orange precipitate. The electronic spectrum of the solution was identical with the known spectrum of fluorenyllithium in the visible region,[31a] and the concentration was 7×10^{-4} *M*.

Ether-free 1,1-diphenyl-*n*-hexyllithium in toluene was prepared in a manner similar to that of Bywater,[10] except that the 1,1-diphenylethylene was distilled off high-vacuum dried KOH pellets to remove any traces of benzophenone. The concentration determined spectrally[10] was 5×10^{-3} *M*. 1,1-Diphenyl-*n*-hexyllithium in THF was prepared by mixing the contents of an ampoule with previously purified and dried THF on a high vacuum line, then distilling off the toluene and THF. Fresh THF was then distilled back onto the residue and the solution was filtered and sealed off into breakseals. On changing solvents, the λ_{max} shifted from 415 to 494 mμ; the molar extinction coefficient for 415 mμ[10] was used at 494 mμ in the determination of the concentration, which was 1.5×10^{-2} *M*.

Lithium tetraphenylboron was prepared from the corresponding sodium salt using the method of Bhattacharyya, *et al.*[47]

Polymerization. Monomer (usually 0.75–1 ml), stabilized with diphenylpicrylhydrazyl, and solvent were dried over CaH_2 at least 24 hr, then distilled onto fresh CaH_2, then after at least 24 hr, the solution was distilled into an ampoule which had fused on it a breakseal. The entire operation was carried out in an all-glass system on a high-vacuum manifold with the usual precautions. The ampoule was then sealed onto a polymerization system on the high-vacuum manifold and packed in Dry Ice until reaction to prevent adventitious polymerization.

Two polymerization techniques were followed, one for monomer concentrations of the order of 1 *M*, the other for more dilute systems. In the former case, when the initiators were not in breakseals, the polymerization system was opened under dry nitrogen and the initiator was introduced through the open side arm, which was then sealed off and the system pumped out. When the initiator was in a breakseal, the standard procedure was followed. After degassing, and, if necessary, distilling away the excess ether, the monomer and solvent were allowed to enter the polymerization ampoule, which was immersed in liquid air and sealed off. The ampoule was then immersed in a Dry Ice bath and allowed to warm to −78° with vigorous shaking. After the polymerization was judged to be complete (usually overnight), the ampoule was opened and the polymerization terminated with water–dioxane or acetic acid in toluene. The solution was transferred to a flask on the high vacuum manifold, frozen, and pumped out, and the volatiles were distilled into another flask. The stripped solvent was then checked by analytical vpc for ether, unreacted monomer, and alcohol owing to carbonyl attack; the concentrations of these were determined from the peak areas and predetermined correction factors. In some cases, the unreacted monomer was then collected with the preparative vpc and checked by nmr for racemization of the β-CHD. In no case was racemization observed.

The dried crude polymer was dissolved in chloroform, precipitated in 15 volumes of petroleum ether in a centrifuge cone, and centrifuged, and the petroleum ether was decanted off. The polymer was then dissolved in chloroform, washed with 0.5 *N* HCl in 50% aqueous methanol, then repeatedly with about 5% aqueous methanol. The polymer was precipitated a second time in petroleum ether and vacuum dried. The polymer was dissolved in benzene, filtered through a fritted-glass filter, freeze dried, then dried under high vacuum for at least 24 hr.

The two petroleum ether fractions were combined, and the petroleum ether was removed under vacuum. The yellow viscous oil was dissolved in chloroform and washed as above, and the chloroform was flashed off. The remaining material was dissolved in benzene, filtered, freeze dried, and vacuum dried.

For those systems which were more dilute, the polymerization vessel had fused on it the monomer and initiator breakseals, a breakseal containing a very small amount of terminating solution, a 2-mm, quartz, optical cell with a 1.9-mm spacer, two capillary viscometers to cover a wide range of viscosities, and in some cases, a conductivity cell. A description and the operation of the conductivity cell is described elsewhere.[31b] After flaming out the system under high vacuum, it was sealed off from the manifold; in a few instances of very low living end concentrations, the system was next washed with a fluorenyllithium solution and rinsed. After the initiator solution was introduced to the system from the breakseal and its concentration checked spectrally, the initiator and the monomer solutions were brought to −78°, then mixed. The polymerization was followed by noting the electronic spectrum and the viscosity increase, as well as the conductivity where applicable. After the viscosity leveled off, the polymerization was terminated, still under vacuum, and the measurements were repeated on the dead solution. Upon termination, the yellow color disappeared, as did the broad indefinite peak which appeared as a shoulder on the toluene peak above 300 mμ.[48] Owing to the experimental difficulties in checking the viscosity in a cold bath, just before termination of one of the runs in ether-free toluene (no. e), the system was allowed to warm to room temperature. The efflux time before and after termination was then determined. In all cases, the efflux times of both the large and small capillary viscometer were recorded. The agreement in the ratio of living to terminated specific viscosities between the two viscometers was better than 4%. Only the data from the larger viscometer are presented in Table I. The polymer was then worked up as before.

Nmr Analysis. The freeze-dried polymer was dissolved in chlorobenzene (14–20% w/v) with TMS, filtered through a Gelman micropore filter into an nmr tube, degassed, and sealed. The spectrum was run on a Varian A-60 at ambient temperature or 150°. The methylene diad[25] and the methyl methacrylate triad[16] analysis have been described before. In the analysis of the methylene tetrads,[39–41] the largest peaks in the predominantly isotactic polymers and syndiotactic polymers were assigned to *mmm* and *rrr*, respectively. The *erythro mmm* peak is considered to be downfield, by analogy to the acrylate polymers.[27,49] The remaining peaks

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(46) G. W. H. Scherf and R. K. Brown, *Can. J. Chem.*, **38**, 2450 (1960).

(47) D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 608 (1965).

(48) D. M. Wiles and S. Bywater, *J. Polymer Sci.*, **B2**, 1175 (1964).

(49) This is not unreasonable, since it has been shown that the long-range shielding of a methyl group is opposite to that of an ester function.[50] When these two are *gauche* or geminal, the effects of long-range shielding are in the same direction. Also the trends in (*tm*)/(*m*) with ether are parallel between the acrylates and the methacrylates for all initiator systems. It seems unlikely that ether would affect the stereochemistry of the two polymers in an opposite manner in every case.

(50) D. J. Patel, M. E. H. Howden, and J. D. Roberts, *J. Am. Chem. Soc.*, **85**, 3216 (1963).

were assigned using a series of free-radical polymers which are known to follow Bernoullian statistics and are therefore predictable.[16,39,51] The consistency relationships between the peak intensities were checked[39] and found to hold. The tetrad ratios were used to calculate the triad ratios in poly(ethyl *cis*-β-d_1-methacrylate).[39] Because the tetrad chemical shift differences were small in the deuterated poly(isopropyl acrylate), it was not possible to calculate tetrad–triad relationships. The reported ratio of *threo–meso* to *meso* has been corrected for the 10% undeuterated monomer in the two methacrylate ester polymer.

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(51) These assignments have been confirmed using a Varian HA-100 and computed average transients on a DP-60 on model compounds. The assignments plus a statistical evaluation of the data to verify the foregoing mechanism will be reported.

Enolene Rearrangements. Relationship to the "Abnormal Claisen Rearrangement" and Other 1,5-Hydrogen Shift Processes[1]

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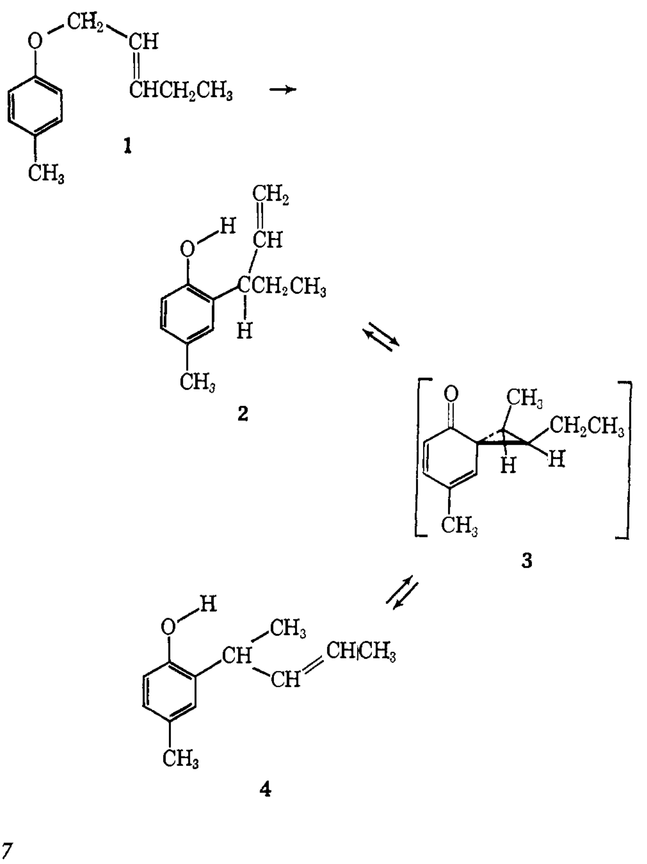
Abstract: Acylalkylcyclopropanes have been shown to undergo clean, facile ring opening upon heating, to produce homoallylic ketones when the acyl and alkyl groups are *cis* (1-acetyl-2,2-dimethylcyclopropane, *cis*-1-acetyl-2-methylcyclopropane), but not when they are *trans* (*trans*-1-acetyl-2-methylcyclopropane). First-order rate constants and the heat of activation of the rearrangement of 1-acetyl-2,2-dimethylcyclopropane to 5-methyl-5-hexen-2-one have been determined. The ring opening and the concerted 1,5-hydrogen shift have been demonstrated to be reversible by following intramolecular deuterium transfers in three homoallylic ketones, 4-pentenophenone, 3-methyl-4-pentenophenone, and 4-methyl-4-pentenophenone, by means of nmr spectroscopy. The lack of deuterium incorporation into the 4-methyl group of the last compound confirmed the intramolecular nature of the transfer of hydrogen to the terminal methylene groups of all three homoallylic ketones. The mechanism of these rearrangements *via* "enolene" intermediates represents an aliphatic analog of the rearrangement of allylic phenols responsible for the "abnormal Claisen rearrangement." The scope of enolene rearrangements and their relationship to other thermal intramolecular rearrangements are discussed.

The "abnormal Claisen rearrangement"[3] has now been clearly identified as the result of two consecutive processes: normal *ortho* Claisen rearrangement of a γ-alkylallyl aryl ether (*e.g.*, **1**) to an *o*-(α-alkylallyl)phenol (*e.g.*, **2**), followed by rearrangement of the side chain of this phenol to produce an isomeric phenol **4**.[4] The mechanism of the secondary rearrangement was formulated as involving a substituted spiro[2.5]octa-4,6-dien-3-one intermediate **3**;[4] recent work has provided strong support for this mechanism.[5,6]

In the present paper we demonstrate that this mechanism is not restricted to allylic phenols but that this



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(1) Preliminary descriptions of this research were given by (a) R. M. Roberts and R. G. Landolt, *J. Am. Chem. Soc.*, **87**, 2281 (1965); (b) R. M. Roberts, R. N. Greene, R. G. Landolt, and E. W. Heyer, *ibid.*, **87**, 2282 (1965); (c) R. M. Roberts and R. G. Landolt, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, Abstracts, p 56S. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society; to the Robert A. Welch Foundation; to the National Science Foundation; and to The University of Texas Research Institute for support of this research.

(2) University of Texas Fellow, 1964–1965.

(3) (a) W. M. Lauer and W. F. Filbert, *J. Am. Chem. Soc.*, **58**, 1388 (1936); (b) W. M. Lauer, G. A. Doldouras, R. E. Hileman, and R. Liepins, *J. Org. Chem.*, **26**, 4785 (1961); (c) A. Habich, R. Barner, W. von Philipsborn, and H. Schmid, *Helv. Chim. Acta*, **45**, 1943 (1962).

(4) E. N. Marvell, D. R. Anderson, and J. Ong, *J. Org. Chem.*, **27**, 1109 (1962).

(5) W. M. Lauer and T. A. Johnson, *ibid.*, **28**, 2913 (1963).

(6) A. Habich, R. Barner, W. von Philipsborn, and H. Schmid, *Helv. Chim. Acta*, **48**, 1297 (1965).