The fractional contributions of the basicity term for the attack of hydroxide ion on the esters is 0.97–0.99; that for the attack of methoxide ion is 0.91; and that for the attack of ethoxide ion is 0.98.

In all cases, the contribution of basicity to the rate of the reaction is very large, indicating that the basicity of the attacking species is the controlling factor in the relative reactivity of such species toward the carbonyl carbon atom of esters. Evidence has been given recently for nucleophilic catalysis in the hydrolysis of esters, by Bender[44] and Bruice.[45] The catalysts studied by these workers showed good correlation with the Brönsted equation and hence basicity of the nucleophile. Basicity again is the controlling factor for reactivity as shown in this investigation, with the exception of the methoxide ion. Apparently the greater polarizability of the methoxide ion is sufficient to reverse the order expected from basicity alone.

Acknowledgment.—The authors gratefully acknowledge valuable discussions with Dr. J. F. Bunnett.

[44] See ref. 45 and M. L. Bender and B. W. Turnquest, THIS JOURNAL, **79**, 1656 (1957).

[45] See refs. 26, 32, 34 and G. L. Schmir and T. C. Bruice, *ibid.*, **80**, 1173 (1958).

CHICAGO 16, ILL.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Anionic Copolymerization of Isoprene and Styrene. I[1]

BY DONALD J. KELLEY AND ARTHUR V. TOBOLSKY

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Lithium, *n*-butyllithium and sodium were used to catalyze the polymerization of equimolar mixtures of isoprene and styrene in various solvents. The compositions of the copolymers initially formed were studied, since this illuminates the nature of the propagation step. Under otherwise similar conditions, the copolymers produced by lithium and by *n*-butyllithium were identical. This is because the propagating species is the ion pair (polymer$^-$Li$^+$) in both cases. In benzene or in undiluted monomers, these catalysts gave copolymers containing somewhat less than 20 weight % styrene. In triethylamine, diethyl ether, and tetrahydrofuran the initial copolymers contained 60, 68 and 80% styrene, respectively. Sodium produces copolymers of 66 weight % styrene in hydrocarbons and from 75 to 80% styrene in ionizing solvents. We deduce that the composition of the copolymers depends mainly on the ionic character of the propagating ($\sim$C$^-$M$^+$) ion pair. A nearly completely free anion gives a copolymer containing 80% styrene. Repressing the ionic character of the complex, by using Li$^+$ rather than Na$^+$ and by using non-ionizing solvents lowers the styrene content. Other factors which might contribute to the observed effect also are discussed.

Introduction

Lithium and alkyllithium-catalyzed polymerizations of isoprene differ markedly from sodium polymerizations in that a stereospecific polymer containing more than 90% of the *cis*-1,4-isomer is produced in bulk and in hydrocarbon solvents.[2-4] In diethyl ether and tetrahydrofuran (THF) stereospecificity vanishes, and polymer containing a mixture of 1,2, 3,4- and *trans*-1,4-structures is obtained.[4,5] Since the nature of the polymerization medium exerts a strong influence on the stereochemistry of the propagation step, the composition of the copolymer initially formed from an equimolar mixture of isoprene and styrene should also depend on the solvent.

In a previous publication,[6] it was shown that, in a particular solvent, the structures of isoprene polymers produced by organometallic initiators like *n*-butyllithium, amyllithium and phenyllithium are not affected by the negatively charged organic fragment of the initiator. This implies that this fragment starts the chain, but that the propagation step is the addition of ($\sim$isoprene$^-$M$^+$) to a monomer double bond. Under otherwise similar conditions the isoprene polymers produced by lithium and by *n*-butyllithium are identical.[3] We believe that metallic lithium first forms a mono- or dialkenyl or an alkyl with the monomer or solvent, which initiates isoprene polymerization in the same manner as does *n*-butyllithium. The propagating species, with both catalysts, is the growing ion pair ($\sim$isoprene$^-$M$^+$). The same is true for sodium and organosodium compounds.

According to the *Q–e* scheme of copolymerization reactivity ratios, the polarity constants (*e*) for butadiene and styrene are both -0.8.[7] Also the reactivities of these two monomers with carbanions are the same.[8] Unfortunately, the *e*-value for isoprene is not published. However, the electron-donating power of the methyl group in isoprene would be expected to produce a lower "*e*-value" than for butadiene and hence also below that of styrene. Thus, an isoprene–styrene copolymer formed by a truly anionic progagation should contain an excess of styrene.

Experimental

Materials.—Phillips Polymerization Grade isoprene, benzene and diethyl ether were refluxed over sodium wire for two hours and fractionally distilled under dry nitrogen just prior to use. Styrene monomer was fractionally distilled under nitrogen at reduced pressure. THF was refluxed over lithium wire and triethylamine (Et$_3$N), over potassium hydroxide before distillation.

n-Butyllithium was prepared in benzene and in diethyl ether in dry helium atmospheres by the methods of Ziegler[9]

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[1] This article is based upon a dissertation submitted by Donald J. Kelley in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Princeton University.

[2] F. W. Stavely, *et al.*, *Ind. Eng. Chem.*, **48**, 778 (1956).

[3] H. Hsieh, D. J. Kelley and A. V. Tobolsky, *J. Polymer Sci.*, **26**, 240 (1957).

[4] H. Hsieh and A. V. Tobolsky, *ibid.*, **25**, 245 (1957).

[5] C. E. Rogers and A. V. Tobolsky, companion manuscript.

[6] H. Morita and A. V. Tobolsky, THIS JOURNAL, **79**, 5853 (1957).

[7] C. C. Price, *J. Polymer Sci.*, **3**, 772 (1948).

[8] G. E. Ham, *ibid.*, **14**, 483 (1954).

[9] K. Ziegler and H. Colonius, *Ann.*, **479**, 135 (1930).

and Gilman,[10] respectively. The solutions were pressure-filtered under dry nitrogen through sintered glass into gasket-sealed bottles of the type described below. The *n*-BuLi concentrations were determined by the double titration method of Gilman.[11] The catalyst prepared in benzene was used in polymerizations carried out in benzene solvent and in undiluted monomers. That prepared in diethyl ether was used in ether, THF and Et_3N.

Lithium metal was supplied by the Lithium Corporation of America as a 30% dispersion in 62% mineral oil and 8% petrolatum with 1% oleic acid stabilizer. A 35% sodium dispersion in white oil #52 with 0.5% aluminum stearate stabilizer was obtained from U. S. Industrial Chemicals Co.

Polymerizations.—Four-ounce, perforated screw-cap bottles were fitted with self-sealing rubber gaskets and charged by pipetting with solvent and monomers in a helium-purged dry-box. A 60:40 weight ratio of styrene:isoprene (equimolar) and a monomer:solvent volume ratio (M:S) of 1:2 were used in all cases. The bottles were then purged of volatile impurities by bubbling through a stream of dry helium for approximately one minute. No evidence of thermal polymerization was observed upon pouring control charges into an excess of methanol. The caps were replaced and the catalyst introduced with a hypodermic syringe after temperature equilibrium had been established. Polymerizations initiated by *n*-BuLi appeared to proceed homogeneously in all solvents used. No solution Tyndall effects were observed on visual examination. Approximately 100 mg. total weight (metal plus oil) of lithium or sodium dispersions and *n*-BuLi concentrations of 1 to 10 millimoles per mole of total monomer were used to initiate polymerization. At least a 100-fold molar excess of solvent over catalyst was used to eliminate any consideration of incomplete solvation of growing chains for stoichiometric reasons. The bottles were magnetically stirred in a bath at 25°. As polymerization proceeded, aliquots were withdrawn through the gaskets *via* syringe and the contents precipitated by pouring into a large excess of methanol containing phenyl-β-naphthylamine as antioxidant. The polymer was reprecipitated at least twice from chloroform and dried *in vacuo* for two days.

All the polymerizations were accompanied by a yellow to red coloring of the solutions, although the appearance of a color did not always signify the formation of polymer. In general the rates of polymerization decreased in the solvent order: THF > diethyl ether > Et_3N > undiluted monomers and benzene, under otherwise similar conditions. Whereas polymerization was instantaneous in THF, the rate decreased to approximately 10% per hour in benzene using *n*-BuLi. Induction periods varying from approximately 15 minutes in ether to several hours in Et_3N and hydrocarbons were found with lithium metal. With sodium, induction periods of several hours were found in Et_3N and benzene, and rates of polymerization were generally greater than for lithium in all solvents. Induction periods and rates were found to be very sensitive to traces of air. Exposure of polymerizing solutions to air resulted in a fading of color and interruption of polymerization.

Analysis.—Copolymers of the various compositions pressed clear, whereas coprecipitated mixtures of homopolymers of the same over-all compositions pressed into opaque films. Cloud point determinations by the addition of methanol to methyl ethyl ketone–benzene solutions of the copolymers[12] failed to show the presence of any isoprene homopolymer in the samples. Free polystyrene also was shown to be absent by fractionation experiments in *n*-heptane, a polyisoprene solvent but a non-solvent for polystyrene. High styrene-content copolymers (approx. 80%) were completely insoluble when extracted with heptane at room temperature, while lower styrene samples (60%) were 90% soluble. The soluble and insoluble fractions had the same composition.

The percentage styrene in the copolymers was determined in chloroform solutions according to the ultraviolet method employed by Meehan for styrene–butadiene copolymers.[13] Butadiene and isoprene have virtually identical absorption spectra in this region. A Warren Spectracord was used to measure transmittance at 269 mμ. Five portions each of several copolymer samples were analyzed by the ultraviolet method and these several specific extinction coefficients were obtained: 0.39 ± 0.020, 0.77 ± 0.036, 1.07 ± 0.043, 1.20 ± 0.049, 1.42 ± 0.100. These values correspond, respectively, to styrene contents of 20.4 ± 1.2%, 42.4 ± 2.3%, 60.0 ± 2.7%, 67.6 ± 2.8% and 80.0 ± 6.0%. Comparisons of values obtained by this method with carbon-hydrogen analysis[14] agree within the limits of precision stated above. We must admit that, at high conversions, some of our results are off as much as 5 and 7% in styrene content. Figures 1 and 5 deviate by these quantities, respectively, from the theoretical styrene content expected at 100% conversion (60.4% styrene), which is shown by a cross on all the figures. Cumulative errors in the pipetting of monomers and in sample recovery are believed to be responsible for errors in excess of the ±2.7% due to the analytical method for samples of 60% styrene.

Results and Discussion

Table I shows the effect of solvent medium on the styrene content (extrapolated to zero conversion) of the copolymers formed by lithium, *n*-butyllithium and sodium catalysis.

TABLE I

PERCENTAGE STYRENE IN ISOPRENE COPOLYMERS AT ZERO CONVERSION

Styrene:Isoprene = 60:40, by weight (equimolar); M:S = 1:2

Solvent	Weight % styrene using Li	*n*-BuLi	Na
Benzene	15 ± 1	18 ± 1	66 ± 3
Undiluted monomers	15 ± 1	17 ± 1	66 ± 3
Et_3N	59 ± 3	60 ± 3	77 ± 6
Diethyl ether	68 ± 3	68 ± 3	75 ± 6
THF	80 ± 6	80 ± 6	80 ± 6

There is a near identity of composition between copolymers initiated by Li and *n*-BuLi systems in each particular solvent, which strengthens the belief that the propagating species is the same in both cases.[15]

In THF, diethyl ether, and triethylamine, the high styrene contents could be explained by the basicities of the solvents, which are able to solvate the Li^+ counterion and dissociate the C–Li bond. In benzene and undiluted monomers the lower styrene content indicates that the propagation step deviates from the simple addition of a "free" polymeric anion to the double bond of a monomer molecule. Figures 1–5 show copolymer composition–conversion curves obtained in the various solvents. Figure 6 is a schematic representation of the data in Table I describing the effects of solvent and catalyst on the composition of initially formed copolymer.

The more covalent nature of the C–Li bond in hydrocarbons does not mean that a free-radical type propagation occurs. Free radicals initiate copolymers containing 80 weight % styrene,[16] while "covalent" C–Li chain ends favor the addition of isoprene monomer. Perhaps isoprene more

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[10] H. Gilman, *et al.*, THIS JOURNAL, **71**, 1499 (1949).

[11] H. Gilman and A. H. Haubein, *ibid.*, **66**, 1515 (1944).

[12] Y. Minoura, Y. Mori and M. Imoto, *Makromol. Chem.*, **24**, 205 (1957).

[13] E. J. Meehan, *J. Polymer Sci.*, **1**, 175 (1946).

[14] Carbon–hydrogen analyses were performed by Mr. George Robertson.

[15] In a previous paper O'Driscoll and Tobolsky found that lithium and *n*-butyllithium give different copolymer compositions for styrene–methyl methacrylate in various solvents. It was proposed that lithium initiates a radical-ion which grows at both ends. In styrene–isoprene systems the radical-ion, if formed, does not grow appreciably at the radical end because of the tendency of the isoprene radicals to couple (K. F. O'Driscoll and A. V. Tobolsky, *J. Polymer Sci.*, **31**, 115, 123 (1958)).

[16] E. Dyer and D. L. Munroe, *J. Am. Chem. Soc.*, **68**, 2726 (1946).

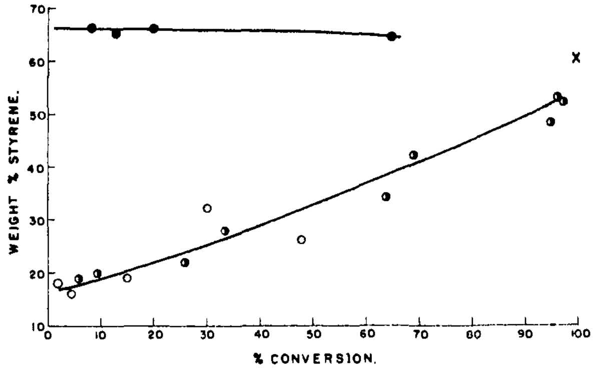

Fig. 1.—Benzene: O, Li; ◑, *n*-BuLi; ●, Na.

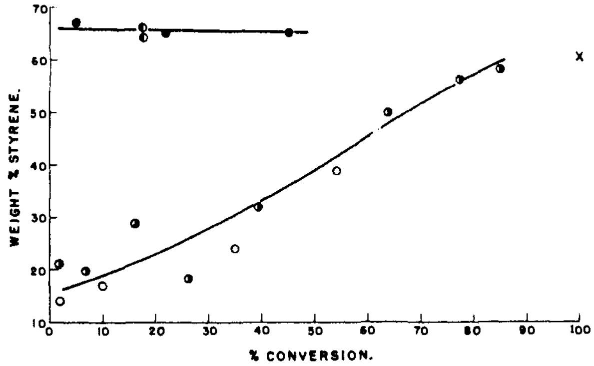

Fig. 2.—Undiluted monomers: O, Li; ●, Na; ◑, *n*-BuLi; ◐, *n*-BuLi (4% ether).

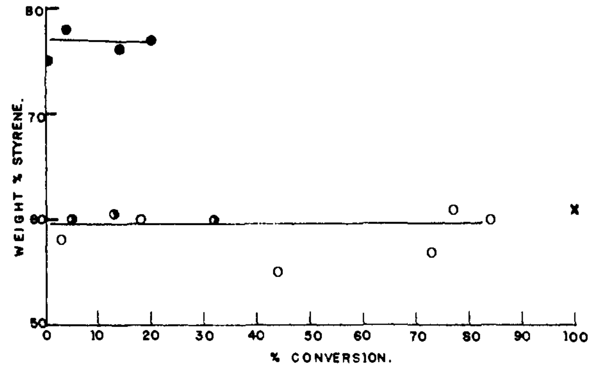

Fig. 3.—Triethylamine: O, Li; ◑, *n*-BuLi; ●, Na.

readily participates in the formation of a transition complex in which the bonds are chiefly covalent. The initial copolymer compositions in hydrocarbon solvents cannot be "explained" by differences in the rates of homopolymerization of styrene and isoprene under the same conditions. The specific rates of the *n*-BuLi-catalyzed homopolymerizations of styrene[17a] and isoprene[17b] in benzene at 20° have been found to be 0.0235 and 0.0035 liters/mole/minute, respectively, whereas a predominance of isoprene is found in the copolymer.

The strong effect of traces of ether on the stereoisomerism of polyisoprene[4,18] is also found in copolymer compositions. When as little as 4%

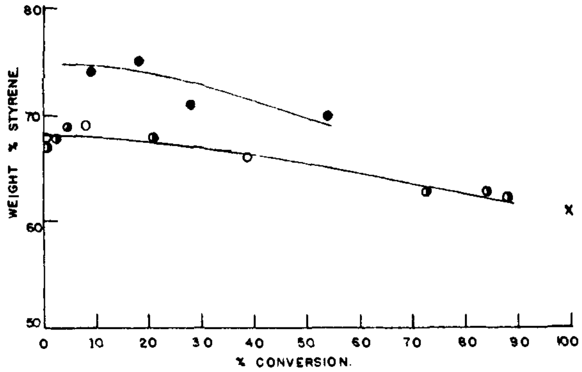

Fig. 4.—Diethyl ether: O, Li; ◑, *n*-BuLi; ●, Na.

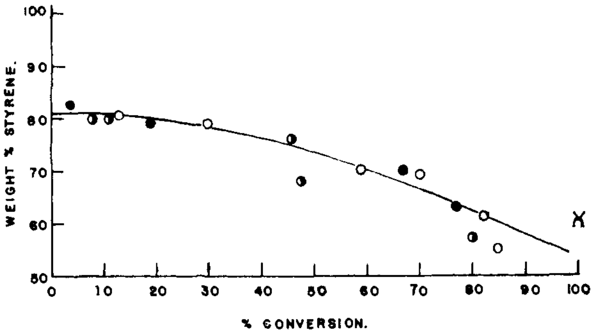

Fig. 5.—THF: O, Li; ◑, *n*-BuLi; ●, Na.

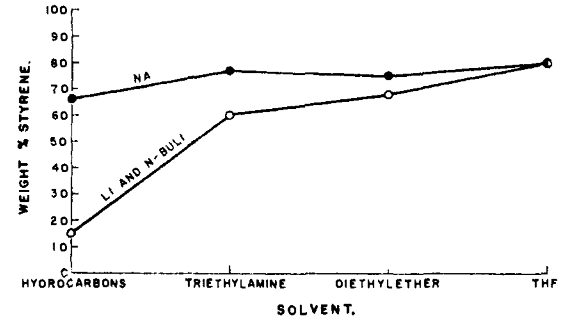

Fig. 6.—Styrene content of initial isoprene copolymers from equimolar feeds.

by weight of diethyl ether is added to a bulk-*n*-BuLi copolymerization mixture, the initial styrene content increases from 17 to 65% (Fig. 2). This indicates that the strong tendency of ether to solvate the Li^+ counterion is more important than a change in dielectric constant or gross solvent basicity.

Sodium produces copolymers whose compositions are less strongly dependent on solvent medium. When the active chain end consists of a C–Na bond, the effective charge separation of the ($\sim C^-$-M^+) pair will be greater than for a C–Li bond because of its greater inherent ionic character in spite of the smaller C–Li bond distance. In benzene and undiluted monomers, ionization of the C–Na bond is not suppressed as much as that of the C–Li bond, and a smaller decrease in styrene content occurs with sodium on passing from ionizing to non-ionizing solvents. In THF the identical compositions of lithium and sodium copolymers indicate that the lithium polymerization has a propagation step similar to the "limiting anionic" case of sodium.

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(17) (a) K. F. O'Driscoll and A. V. Tobolsky, *J. Polymer Sci.*, in press; (b) H. M. Whitacre, C. E. Rogers and A. V. Tobolsky, Senior Thesis of H. M. Whitacre, Princeton University, 1958.

(18) H. E. Diem, H. Tucker and C. F. Gibbs, Rubber Div., 132nd Meeting, Am. Chem. Soc., New York, Sept., 1957.

In any given solvent–catalyst system no effect on the styrene content was observed by varying the monomer:solvent volume ratio (M:S) between 1:1 and 1:5. Also in the *n*-BuLi systems no effect was produced by varying the catalyst concentration between 0.6 and 2.0 mg./ml. or between catalyst: monomer mole ratios of 1:1000 and 1:100.

In an effort to detect a tendency to form blocks of one monomer type in a given chain, traces of one particular kind of monomer were initiated by *n*-BuLi prior to the addition of the gross comonomer–solvent mixture. No significant differences in the copolymer compositions were found by varying the initiating monomer from styrene to isoprene.

In assessing the effect of a solvent on its ability to ionize the $(\sim C^-Li^+)$ ion pair, such factors as complexing ability, dielectric constant, and base or acid strength should be taken into account. The results are too meager to give a quantitative account at this point. Similar considerations have also been suggested for cationic copolymerizations.[19]

Although electrical effects, such as the degree of ionization, appear to play a very important role, we cannot rule out the possible influence of steric factors. Monomer molecules could, for example, be oriented by interaction with associated organometallic species of the type $(RLi)_n$ before adding to the growing chain. These association complexes may possibly act like tiny "surfaces," even though the solutions appear clear.[6,20] The existence of such association complexes is well known; for example, *n*-butyllithium is known to be associated to degrees of 5 and 7 in diethyl ether and benzene, respectively.[21] Other specific structures of the transition complex between propagating ion pair and adding monomer, such as ring structures, may also affect the copolymer composition.

(19) R. E. Florin, THIS JOURNAL, **73**, 4168 (1951).

(20) G. Natta, International Meeting on Chemistry of Coördination Compounds, Rome, Sept., 1957.

(21) G. Wittig, F. J. Meyer and G. Lange, *Ann.*, **571**, 167 (1951).

PRINCETON, N. J.

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

Mechanisms of Elimination Reactions. XX. Reactions of 2-Bromocyclohexanols and Derivatives with Zinc[1]

BY STANLEY J. CRISTOL AND LEO E. RADEMACHER

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Relative rates of reaction of the *cis* and *trans* isomers of 2-bromocyclohexanol, 2-bromocyclohexyl acetate and 2-bromocyclohexyl *p*-toluenesulfonate in absolute ethanol with zinc–copper couple have been determined. A significant difference in reactivity between isomeric pairs exists only in the case of the *p*-toluenesulfonates, the *trans* isomer reacting about 10 times as fast as the *cis* isomer.

Several reports[2] during the past few years have indicated that reactions of 1,2-bromohydrins and simple derivatives with zinc can be used to introduce double bonds into cyclic compounds regardless of whether the groups are in the *cis* or *trans* position. While no detailed study of the relative rates of reaction of stereoisomeric pairs has been reported, reaction conditions were usually quite similar. Since it was known that elimination reactions of 1,2-dibromides show a strong tendency to take the *trans* course,[3] it seemed likely that some difference in reactivity might be found in the case of *cis*- and *trans*-1,2-bromohydrins and simple derivatives thereof. We therefore undertook a study of eliminations from these compounds with zinc–copper couple and with iodide ion. The iodide-ion promoted elimination studies have been reported previously.[4] Since the completion of this work, House and Ro[5] have reported data which indicate a complete lack of preference for either the *cis* or *trans* elimination route in certain acyclic *β*-bromoalkyl acetates and methyl ethers.

We have determined the relative rates of reaction of *cis* and *trans* isomers of 2-bromocyclohexanol (I), 2-bromocyclohexyl acetate (II) and 2-bromocyclohexyl *p*-toluenesulfonate (III) with zinc–copper couple by refluxing solutions of the compounds in absolute ethanol or glacial acetic acid over granular, copper-sulfate-treated zinc for various lengths of time and then determining the yields of cyclohexene and bromide ions. The results are summarized in Table I.

Also, large samples of *cis*- and *trans*-2-bromocyclohexanol were heated at reflux in ethanol over zinc–copper for 81 hours after which the organic products were separated by ether extraction, fractionally distilled, and converted to suitable derivatives. From the *cis* compound we isolated 8% cyclohexanol, 1% *trans*-2-ethoxycyclohexanol and 39% cyclohexene. From the *trans* isomer we obtained 11% *trans*-2-ethoxycyclohexanol and 46% cyclohexene, but were unable to detect any cyclohexanol. In both cases there were small amounts of tars which could not be distilled without decomposition.

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(1) Previous paper in series: S. J. Cristol and R. P. Arganbright, THIS JOURNAL, **79**, 3441 (1957). This work was reported at the Fourteenth National Organic Symposium, Lafayette, Ind., in June, 1955.

(2) See for example: (a) L. F. Fieser and R. Ettorre, *ibid.*, **75**, 1700 (1953); (b) D. R. James, R. W. Rees and C. W. Shoppee, *J. Chem. Soc.*, 1370 (1955); (c) L. Crombie and S. H. Harper, *ibid.*, 1705, 1715 (1950); (d) L. Crombie, J. Gold, S. H. Harper and B. J. Stokes, *ibid.*, 136 (1956).

(3) (a) W. G. Young, Z. Jasaitis and L. Levanas, THIS JOURNAL, **59**, 403 (1937); (b) W. G. Young, S. J. Cristol and T. S. Skei, *ibid.*, **65**, 2099 (1943).

(4) S. J. Cristol, J. Q. Weber and M. C. Brindell, *ibid.*, **78**, 598 (1956).

(5) H. O. House and R. S. Ro, *ibid.*, **80**, 182 (1958).