

due to some attack of ozone on the solvent rather than to the presence of hydroperoxides VI and VII. The reaction mixtures were then worked up and the products determined precisely as described for the hydroperoxide (VI) decompositions in the accompanying paper.⁵ The results are shown in Table I.

Ozonolysis of diphenylacetylene (IIe). a) *Attempt to isolate a hydroperoxide.* The ozonolysis was carried out in methanol at -15° as described for the other acetylenes. Using the procedure described earlier, no crystalline hydroperoxide could be isolated. This was also true for ozonolysis of IIe in a 1-4 methanol-carbon tetrachloride mixture at -20° .

b) *Ozonolysis and thermal decomposition.* The ozonolysis was carried out in methanol at -20° as described in preceding experiments. The reaction mixture was refluxed for 15 min., after which the methanol was removed under reduced pressure. The residue was treated with excess sodium bicarbonate solution and the resulting mixture was extracted six times with ether. The ether extract was evaporated under reduced pressure and the residue was distilled giving an 86% yield of methyl benzoate (b.p. $90-95^{\circ}/15$ mm.), which was identified by gas chromatographic techniques. The remaining residue crystallized

from petroleum ether, giving a 9% yield of benzoic anhydride, m.p. $41-42^{\circ}$, identification by the mixture melting point method. The sodium bicarbonate extract was acidified with conc. hydrochloric acid, cooled, and filtered. The filtrate was extracted six times with ether and the ether extract was evaporated. Benzoic acid was obtained from these operations in 71% yield, m.p. $121-122^{\circ}$, identification by the mixture melting point method.

c) *Ozonolysis and reduction* was carried out as described in preceding experiments. Work-up as described in the immediately preceding experiment gave 16% benzoic acid and 15% methyl benzoate. The final residue was benzil (72% yield, m.p. $95-96^{\circ}$). Crystalline materials were identified by the mixture melting point method and methyl benzoate by gas chromatography.

Acknowledgment. The authors are grateful for grants from the Robert A. Welch Foundation (F-042) and the National Science Foundation (G-7353) which made this work possible.

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

Alternation Copolymerization

MICHAEL M. MARTIN AND NORMAN P. JENSEN

Received October 12, 1961

3-Phenylpropene-1, 4-phenylbutene-1, and 5-phenylpentene-1 have been found to form perfect alternating copolymers of relatively high molecular weight with maleic anhydride. An explanation for alternation copolymerization based upon interactions of dipoles in the radical and double bond is believed to be more consistent with these findings than the more generally expounded explanation which call for transition state stabilization by electron transfer.

One of the most interesting aspects of free radical chemistry is the tendency of certain monomer pairs to form alternating copolymers.¹⁻⁴ Styrene and maleic anhydride provide an excellent example of such a system. A copolymer is produced which is composed of equivalent amounts of each monomer, regardless of initial monomer concentrations, arranged along the chain in regularly alternating fashion. Alternating copolymers of maleic anhydride, which homopolymerizes only to a very limited degree under conditions of free radical initiation, with other monomers which readily homopolymerize, such as vinyl chloride, vinyl acetate, and isopropenyl acetate, have also been reported.⁵

Equally interesting is the formation of relatively high molecular weight alternating copolymers from maleic anhydride and monomers which will not

readily homopolymerize. Such terminal olefins as propylene,^{6,7} diisobutylene,^{7,8} octene,⁹ dodecene,¹⁰ and some allylsilanes¹¹ have been reported to copolymerize with maleic anhydride under conditions of free radical initiation, apparently to alternating copolymers. The most thorough study of such a system was by Bartlett and Nozaki.¹² They found that the kinetic chain length for the copolymerization of allyl acetate and maleic anhydride is 36,000, whereas for allyl acetate alone it is 36.4, for maleic anhydride alone, 29.

The failure of monomers possessing allylic hydrogens to form high molecular weight homopolymers through a free radical process is due to chain transfer with monomer. The growing polymer

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(2) F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950).

(3) G. M. Burnett, "Mechanism of Polymer Reactions," Interscience Publishers, Inc., New York, 1954, Chap. 8.

(4) T. Alfrey, J. J. Bohrer, and H. Mark, "Copolymerization," Interscience Publishers, Inc., New York, 1952.

(5) M. C. deWilde and G. Smets, *J. Polymer Sci.*, **5**, 253 (1950).

(6) W. E. Hanford, U. S. Patent **2,396,785**, March 19, 1946.

(7) W. E. Hanford, U. S. Patent **2,378,629**, June 19, 1945.

(8) R. M. Thomas and W. J. Sparks, U. S. Patent **2,373,067**, April 3, 1945.

(9) J. J. Gianmaria, U. S. Patent **2,698,316**, December 16, 1954.

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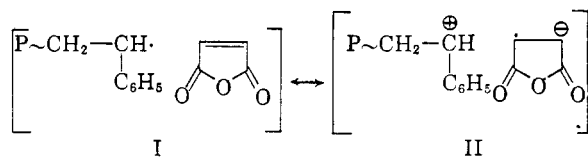
(11) Libby Owens Ford Glass Co., Brit Patent **663,770**, December 27, 1951.

(12) P. D. Bartlett and K. Nozaki, *J. Am. Chem. Soc.*, **68**, 1495 (1946).

chain is terminated early in its existence by abstraction of a labile allylic hydrogen from the monomer, giving a new radical which is too stable to initiate a new chain.^{1,13,14} Thus it must be concluded that when such a monomer copolymerizes with maleic anhydride, the cross-propagation step is able to compete very effectively with such allylic termination, as high molecular weight polymers are produced.

Price¹⁵⁻¹⁸ explained alternation in terms of monomer and radical polarity, stating that substituents attached to the double bond or radical center lead to electron-rich and electron-poor centers, the interaction of which increases or decreases the energy required for the two species to react. This view has been criticized by Walling¹ and Mayo,¹⁹ who state that such an explanation would require that reactivity ratio products should depend upon the dielectric constant of the solvent, which is found not to be the case. Price,²⁰ in turn, has challenged this criticism by pointing out that the extent to which the dielectric constant affects the reactivity ratio product depends upon the model chosen for the transition state, and he chooses one in which the dipoles do not interact until they are within 2 or 3 Å of one another, in which case the effective dielectric constant is independent of solvent.

The views of Price have largely been superseded by those of Walling.^{1,21,22} The essential feature of Walling's proposal is that transition state stabilization results from electron transfer between radical and olefin. Thus, the transition state for the addition of the styryl radical to maleic anhydride is depicted as deriving stabilization through the participation of canonical form II, derived by formal donation of an electron by the styryl radical to the maleic anhydride. Similarly, the transition state for the addition of the radical



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(14) P. D. Bartlett and R. Altshul, *J. Am. Chem. Soc.*, **67**, 816 (1945).

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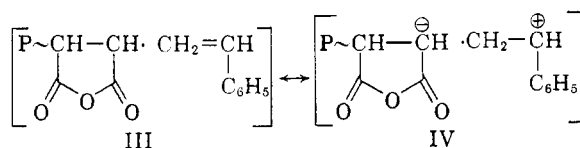
(19) C. Walling and F. Mayo, *J. Polymer Sci.*, **3**, 895 (1948).

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(22) C. Walling, D. Seymour, and K. B. Wolfstirn, *J. Am. Chem. Soc.*, **70**, 1544 (1948).

derived from maleic anhydride to styrene can derive stabilization through participation of canonical form IV. The transition states are stabilized by the participation of structures which partake of the electronic characteristics of benzyl cations and enolate anions, relatively stable entities.



In this paper it is reported that 3-phenylpropene-1, 4-phenylbutene-1, and 5-phenylpentene-1 form relatively high molecular weight alternating copolymers with maleic anhydride. These three monomers, possessing both allylic and benzylic hydrogens, should be particularly prone toward degradative chain transfer. It is felt that their behavior is more in concert with Price's views on the origin of alternation than with Walling's.

EXPERIMENTAL

Materials. Maleic anhydride was purified by recrystallization from a 1:1 carbon tetrachloride-chloroform mixture.

3-Phenylpropene-1, b.p. 154.5°-155.0°, was prepared according to the procedure described by Hershberg²³ from phenylmagnesium bromide and 3-bromopropene-1.

4-Phenylbutene-1, b.p. 176.5°-177°, was prepared similarly in 70% yield from benzylmagnesium chloride and 3-bromopropene-1.

5-Phenylbutene-1, b.p. 78.5°-79.0°/11 mm., was prepared from 2-phenylethylmagnesium bromide and 3-bromopropene-1.²⁴

Copolymerizations. The bulk copolymerizations were carried out under nitrogen in small pressure bottles at 59.6 ± 0.2° to conversions of 5 to 15%, using azobisisobutyronitrile (0.1 mole %) as initiator.

Copolymers of 3-phenylpropene-1 or 5-phenylpentene-1 and maleic anhydride were purified by dissolving the polymerization mixture in dioxane and pouring the solution into ether to bring about precipitation. The polymers were reprecipitated three times from dioxane into ether, and finally dissolved in dioxane, treated with activated carbon if the solutions were discolored, and "freeze-dried." The composition of the polymers was determined by ultimate analysis.

The copolymers of 4-phenylbutene-1 and maleic anhydride are apparently of higher molecular weight than those from the other two olefins, and are less soluble in dioxane. A 3:1 mixture of tetrahydrofuran-dioxane was used to dissolve the polymers. Five reprecipitations did not succeed in removing all of the unchanged maleic anhydride from the polymers, however, and carbon analyses were erratic and invariably lower than calculated for an alternating copolymer. Pure polymers were obtained by dissolving the thrice reprecipitated copolymers in a 2:1 mixture of tetrahydrofuran:water and heating at 60° for 10 hr. to hydrolyze the anhydride groups. Pouring the hydrolysis mixture into ether caused the polymers to precipitate as sticky, tacky masses. Solvent was decanted, and the gummy residues dissolved in dioxane and "freeze-dried." Composition of the copolymers was then determined by titration with 0.1000 *N* sodium hydroxide

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(24) J. von Braun, H. Deutsch, and A. Schmatloch, *Ber.*, **45**, 1246 (1912).

solution, 2:1 dioxane-water serving as solvent for the polymer sample.

Viscosities were measured in dimethylformamide using a Cannon-Fenske viscosimeter.

RESULTS

From Tables I, II, and III the composition of a copolymer from the binary systems 3-phenylpropene-1-maleic anhydride, 4-phenylbutene-1-maleic anhydride, and 5-phenylpentene-1-maleic anhydride is seen to be independent of monomer feed ratio and to consist of equal parts of maleic anhydride and ω -phenylalkene. All three systems form alternating copolymers.

TABLE I
COPOLYMERS OF MALEIC ANHYDRIDE
AND 3-PHENYLPROPENE-1

Molar Ratio of Monomer Feed, Maleic Anhydride- 3-Phenyl- propene-1	Analysis of Polymer		Composition of Polymer ^a	
			Mole % Maleic Anhydride Incorpo- rated	Mole % 3-Phenyl- propene-1 Incorpo- rated
	% C	% H		
1:3	70.84	5.73	53	47
1:2	71.28	5.68	52	48
1:1	70.81	5.51	53	47
2:1	71.08	5.66	52	48
3:1	70.96	5.70	53	47

^a Calculated from carbon analysis.

TABLE II
COPOLYMERS OF MALEIC ANHYDRIDE AND
4-PHENYLBUTENE-1

Molar Ratio of Monomer Feed, Maleic Anhydride- 4-Phenylbutene-1	Composition of Polymer ^a	
	Mole % maleic anhydride incorporated	Mole % 4- phenylbutene-1 incorporated
1:2	49	51
1:1	48	52
2:1	48	52

^a Determined by hydrolyzing the anhydride units to dicarboxylic acid residues, and titrating with 0.1000 N NaOH.

TABLE III
COPOLYMERS OF MALEIC ANHYDRIDE
AND 5-PHENYLPENTENE-1

Molar Ratio of Monomer Feed, Maleic Anhydride- 5-Phenyl- pentene-1	Analysis of Polymer		Composition of Polymer ^a	
			Mole % Maleic anhydride incorpo- rated	Mole % 5-Phenyl- pentene-1 incorpo- rated
	% C	% H		
1:3	72.41	6.55	53	47
1:2	72.50	6.35	53	47
1:1	72.43	6.31	53	47
2:1	72.18	6.30	53	47
3:1	72.68	6.64	52	48

^a Calculated from carbon analysis.

In Table IV are collected data on yields and solution viscosities of copolymers of maleic anhydride with 3-phenylpropene-1, 4-phenylbutene-1, and 5-phenylpentene-1. Although constants were not evaluated for relating viscosity and molecular

TABLE IV
BULK COPOLYMERIZATIONS OF MALEIC ANHYDRIDE WITH
 ω -Phenylalkenes (59.6°)

Alkene ^a	Time, Hr.	Yield, %	η^b
Styrene	0.5	54	0.48
3-Phenylpropene-1 ^c	3.0	7	0.02
4-Phenylbutene-1 ^c	3.0	24	0.15
5-Phenylpentene-1 ^c	3.0	14	0.10
Octene-1 ^d	3.0	0	—

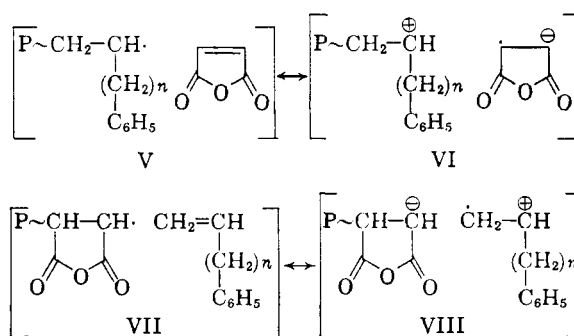
^a Maleic anhydride-alkene = 1.00:1.00, 0.1 mole % AIBN initiator. ^b Inherent viscosities measured in dimethylformamide at 24.9° using a Cannon-Fenske viscosimeter. ^c Does not homopolymerize. ^d Heterogeneous.

weights, it is possible to estimate that the copolymers derived from 4-phenylbutene-1 and 5-phenylpentene-1 have molecular weights of the order of 20,000 whereas the one derived from 3-phenylpropene-1 is probably less than 5,000.

DISCUSSION

The three ω -phenylalkenes, 3-phenylpropene-1, 4-phenylbutene-1, and 5-phenylpentene-1, all of which fail to homopolymerize, readily copolymerize with maleic anhydride to relatively high molecular weight alternating copolymers. This means that the ratio of the rate constants for each of the cross-propagation steps to the rate constant for allylic termination is much larger in the copolymerizing system than is the corresponding ratio in the homopolymerizing system, that is, cross-propagation competes effectively with allylic termination whereas propagation involving like monomer and radical does not.

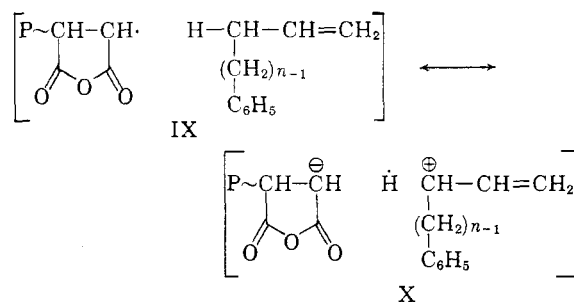
In terms of Walling's explanation for alternation, transition state stabilization must result from electron transfer from the radical derived from the ω -phenylalkene to the maleic anhydride, or from the ω -phenylalkene to the radical derived from maleic anhydride. The charge transfer structures



for the cross-propagation steps are represented by VI and VIII. Clearly, these structures are not as favorable as the corresponding ones for styrene-maleic anhydride (II and IV), because the cationic structure resembles a simple secondary alkyl carbonium ion, which does not exhibit any special stabilizing features. Most of the stabilization derived from the participation of electron transfer structures VI and VIII must then be attributed to the enolate-like part. As structures VI and VIII are less stable than II and IV, it can be concluded that the enhancement of cross-propagation relative to propagation involving like radical and monomer is greater in the case of styrene-maleic anhydride than in the systems described in this paper.

The possibility of bridging by the phenyl group must be considered as a possible means by which structures V-VIII might derive stability. Aryl participation has been observed in certain solvolytic reactions in which a phenyl group is two or four atoms removed from the leaving group.²⁵ In radical forming reactions such participation seems unlikely, however, in light of the evidence which has been presented against the existence of bridged radicals.^{26,27} Furthermore, in the case of 4-phenylbutene-1, the positive charge would be three atoms removed from the benzene ring, and aryl participation has been found not to be operative during the solvolysis of 3-phenylpropyl brosylate. Consequently, it is highly unlikely that the cationic part of the charge transfer structures VI and VIII derive stability through the formation of bridged, "nonclassical" structures.

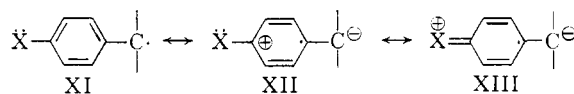
It is also necessary to consider allylic termination in the copolymerizing system. Using the notion of electron transfer as a means of stabilizing transition states in free radical reactions, the conclusion is unavoidable that degradative chain transfer involving the ω -phenylalkene and the radical derived from maleic anhydride should be very favorable. Structure X represents the canonical form derived from electron transfer contributing to the stabilization of the transition state for abstraction of an allylic hydrogen from a phenylalkene by the radical derived from maleic anhydride. An analogous structure can be written for abstraction of a benzylic hydrogen. Structure X is of comparable stability to II and IV and much more stable than VI and VIII, because the cationic portion resembles a stable allylic or benzylic cation. Thus, it follows that crossed allylic termination should be enhanced to a greater extent than cross-propagation, and that degradative chain transfer should compete more effectively with



propagation in the copolymerizing system than in the homopolymerizing system. This is clearly contradicted by the experimental results.

We feel that it is possible to arrive at a more consistent interpretation of the polar effects operating in free radical-forming reactions by concentrating on two factors, stability of the product radical and interactions of reactant dipoles, and that no reference need be made to electron transfer in the transition state.

For highly exothermic processes, for which the activation energy is small, the transition state more closely resembles reactants than products.²⁸ Such a process is free radical addition to a double bond. Thus it is quite legitimate to focus attention on interactions of reactants. Maleic anhydride has a very strong dipole with the positive end toward the double bond. Likewise, a radical adjacent to a carbonyl group will be electron poor, that is, it will be the positive end of a dipole. A simple olefin, on the other hand, is not very polar, there being only a weak dipole with the negative end toward the double bond, resulting from differences in electronegativities of the sp^2 and sp^3 carbon atoms. A simple alkyl radical, however, is probably somewhat more polar in character, the radical carbon being the negative end of a dipole. Recently, Taft²⁹ has suggested that the enhanced resonance effect observed for *para* substituents in reactions leading to the formation of benzyl radicals is a result of polar contributing forms such as XII and XIII. This suggests that benzyl radicals are strong dipoles with the negative end at the radical carbon. The



same is true of any simple alkyl radical to a somewhat lesser extent, due to inductive release by groups attached to the radical carbon.

In a copolymerizing system of alkene and maleic anhydride, the reaction of the electron-rich radical derived from the alkene with the electron-poor double bond of maleic anhydride is more favorable than the reaction with the double bond of another alkene molecule. Also the reaction of the electron-

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poor radical derived from maleic anhydride with the slightly electron-rich double bond of the alkene is more favorable than the reaction with the electron-poor double bond of maleic anhydride. Thus, the enhanced favorability of propagation steps involving unlike radical and monomer relative to steps involving like radical and monomer follows logically. But using this approach, the conclusion does not follow that crossed allylic termination should also be enhanced. In fact the energy of activation for abstraction of an allylic or benzylic hydrogen by a radical derived from maleic anhydride would be predicted to be greater than that for abstraction by the radical derived from the phenylalkene. To the extent that polar interactions of reactants influence the activation energy, reaction of the electron-poor radical derived from maleic anhydride with allylic or benzylic hydrogens will be rendered less favorable by the inductive withdrawal on the part of the vinyl or phenyl group, leading to a lowering of the electron density in these bonds. To the extent that the transition state resembles products, the activation energy for the reaction involving the radical adjacent to a carbonyl group will be larger than that involving the secondary alkyl radical, because the former is a more stable radical and its destruction results in a correspondingly larger loss of resonance energy.

Thus, in a copolymerizing system of maleic anhydride and an alkene, propagation steps involving unlike radical and monomer are greatly

enhanced, while allylic termination involving unlike radical and monomer is diminished in importance. These are the conditions necessary for the production of a high molecular weight polymer.

We feel that the many polar effects which have been reported in free radical forming reactions^{1,21,22,30-35} can all be interpreted more simply in terms of polar interactions of reactants for low activation energy processes in which the transition state resembles reactants, or radical stability, the polar character of the radical being recognized,²⁹ for higher activation energy processes in which the transition state partakes of more of the character of the product radical; and that the postulate of transition state stabilization by electron transfer is unnecessary and in some cases leads to invalid predictions.

Acknowledgment. This research was supported in part by funds made available to this department by E. I. du Pont de Nemours Co.

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[CONTRIBUTION FROM MONSANTO CHEMICAL CO.]

Chlorination with Cupric Chloride

R. P. ARGANBRIGHT AND W. F. YATES

Received October 30, 1961

The reaction of pumice-supported cupric chloride with olefins was studied under temperature conditions which allowed the formation of dichlorides. The relative rates of reaction of various olefins and the stereochemistry of the products indicate that cupric chloride gives nonconcerted, stereospecific *trans* addition of chlorine to simple olefins. Homoconjugative addition was obtained with cupric chloride and norbornadiene.

The reaction of cupric chloride with hydrocarbons has been extensively studied at high temperatures (above 400°). Under such conditions the chlorine evolution from a copper chloride melt (containing potassium chloride) was found to be rate determining and the products obtained were those expected from a free radical chlorination,¹ for example, the reaction of methane to form methyl chloride.

We have been interested in the chemistry of the reaction of supported cupric chloride and olefins

in a lower temperature range (220–330°) in which addition rather than substitution reactions occur.² For our study of the reaction, cupric chloride was supported on 40- to 100-mesh pumice and fluidized with nitrogen during its reaction with the olefin. The use of a fluid bed for the reaction allowed good temperature control, while the use of pumice allowed us to study the copper chloride reaction without the complicating effects of the more adsorbing and reactive supports such as the aluminas.

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