description is somewhat less specific as to origin of the effect. This is more or less the equivalent of Dewar's conclusion that if the conjugated interaction between the substituent and the ring (as measured by the magnitude of the size of the resonance and overlap integrals) is large enough, the compounds in question will show preferential *ortho* orientation despite the differential increase in the electron affinity of the *o*-carbon atom. One is reluctant to assign significant weight to structures such as III and IV because of the obvious electrostatic complications. Similarly, the significance of the naive MO picture may be questioned since the theory does not attempt to correlate the π-electrons in the many electron system.

It is our view that the experimental evidence points clearly to the conclusion that there is some measurable gain derived from maintaining the conjugate interaction between the substituent and the ring in the transition states involved in electrophilic substitution reactions. Since this is true in benzonitrile, it must also be true of related nitro- and carboxyl-substituted compounds. The steric effect which was suggested previously[5] may play a significant role, but there is no direct evidence to support such a view. The separation of steric and electronic effects in these systems appears to be a rather formidable problem.

Acknowledgments.—The authors wish to thank the Iowa State Institute for Atomic Research for the use of the infrared spectrophotometers and Mr. Robert McCord who ran many of the spectra.

AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, CASE INSTITUTE OF TECHNOLOGY]

Cross-linking of Polymers with Dimaleimides[1]

BY PETER KOVACIC AND RICHARD W. HEIN

RECEIVED AUGUST 8, 1958

From gelation and compounding studies, dimaleimides were found to cross-link a wide variety of polymers including unsaturated hydrocarbon types, polyethylene, polymers containing amino groups and a urethan polymer. Except for the amino-containing polymers, the presence of catalytic amounts of peroxide was necessary for effective cross-linking. The chemistry of the cross-linking processes is discussed.

Introduction

Dimaleimides represent a recent addition[2] to the group of compounds which cross-link polymers. This report is concerned with the versatility of dimaleimides as cross-linking agents for various types of polymers and with the chemistry of the reactions involved.

Results and Discussion

The dimaleimides were synthesized according to the method[3] of Searle. In general, a diamine was condensed with maleic anhydride to give the corresponding dimaleamic acid which upon elimination of water yielded the dimaleimide (I).

$$\begin{matrix}\text{CHCO}\\ \|\\ \text{CHCO}\end{matrix}\!>\!\text{NRN}\!<\!\begin{matrix}\text{COCH}\\ \|\\ \text{COCH}\end{matrix}$$

(I)

From gelation and compounding studies, dimaleimides were found to cross-link a wide variety of polymers including unsaturated hydrocarbon types, polyethylene, polymers containing amino groups and a urethan polymer.

Unsaturated Hydrocarbon Polymers.—In the literature many types of compounds are reported as cross-linking agents for unsaturated polymers, particularly natural rubber. Of these reagents, sulfur–accelerator combinations and peroxides are the best known and most useful.

Gelation studies (Table I) in *o*-dichlorobenzene showed that N,N'-*m*-phenylenedimaleimide (5% by weight based on the polymer) readily cross-linked natural rubber at 108-150° in the presence of catalytic amounts of dicumyl peroxide or benzoyl peroxide. When either the dimaleimide or dicumyl peroxide was decreased in amount by 80%, no

TABLE I

NATURAL RUBBER, N,N'-*m*-PHENYLENEDIMALEIMIDE AND PEROXIDES: GELATION STUDIES[a]

MPD, g.[b]	Dicumyl peroxide, g.	Benzoyl peroxide, g.	Extent of gelation	Temp., °C. Gelation	Temp., °C. Maximum
5	0.5	..	Good	125–128	131
5	.25	..	Fair	142–144	144
5	.1	..	None	.....	177
2	.5	..	Good	141–150	173
2	.25	..	Fair	148	152
2	.1	..	None	.....	179
1	.5	..	None	.....	160
5	..	..	None	.....	176
..	.5	..	None	.....	177
..	..	..	None	.....	173
5[c]	.5	..	None	.....	175
5	..	0.5	Good	108–109	113
5	..	.25	Good	109	109
5	..	.1	None	.....	150
..	..	.5	Slight	100–110	178
..	..	.25	None	.....	150

[a] Weights are based on 100 g. of pale crepe as a 3% solution in *o*-dichlorobenzene. [b] MPD = N,N'-*m*-phenylenedimaleimide. [c] No natural rubber present.

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[1] Paper 1 in the series "New Cross-linking Agents for Polymers." This paper was presented at the 134th Meeting of the American Chemical Society in Chicago, Ill., September, 1958, and is in part an abstract of a portion of the M.S. thesis of R. W. Hein, Case Institute of Technology, 1958.

[2] P. Kovacic, U. S. Patent 2,818,405 (1957); *C. A.*, **52**, 5018 (1958).

[3] N. E. Searle, U. S. Patent 2,444,536 (1948); *C. A.*, **42**, 7340 (1948); H. W. Arnold and N. E. Searle, U. S. Patent 2,462,835 (1949); *C. A.*, **43**, 4421 (1949).

insolubilization resulted. Control experiments with 5% of the dimaleimide or 0.5% of dicumyl peroxide demonstrated conclusively the necessity of the combination for effective gelation.

An analogous situation prevailed in the cross-linking of GR-S with N,N′-*m*-phenylenedimaleimide and dicumyl peroxide (Table II).

A more detailed study of cross-linking involving unsaturated hydrocarbon polymers with this system is reported elsewhere,[4] including a discussion of the chemistry involved.

Polyethylene.—In a similar manner, low density polyethylene was converted to gel by heating to 177° in *o*-dichlorobenzene (Table II). Good gelation could be effected with 4% of the dimaleimide and 0.4% of dicumyl peroxide. Insufficient information is at hand to permit a choice among the structural features of polyethylene (methylene groups, *t*-hydrogen positions and unsaturation) as to which participates in the cross-linking process. Relevant to this is the report[5] of Farmer and Moore that saturated hydrocarbons, *e.g.*, cyclohexane, are attacked by *t*-butoxy radicals at 140°.

High density polyethylene and polypropylene were converted to gel at about 100° in the absence of added ingredients.

TABLE II

GR-S, POLYETHYLENE AND NEOPRENE WITH N,N′-*m*-PHENYLENEDIMALEIMIDE AND DICUMYL PEROXIDE: GELATION STUDIES[a]

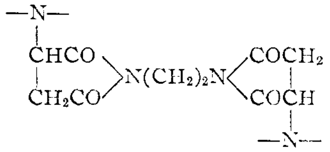
Polymer	MPD, g.[b]	Dicumyl peroxide, g.	Extent of gelation	Temp., °C. Gelation	Temp., °C. Maximum
GR-S-1500[c]	4.0	0.4	Good	145–148	148
GR-S-1500	4.0	..	None	.....	178
GR-S-1500	..	.4	Slight	150–159	179
Polyethylene[d] (low density)	4.0	.4	Good	177	177
	4.0	..	None	.....	178
Polyethylene[d] (low density)	..	.4	None	.....	176
Polyethylene[e] (high density)	..	..	Fair	97	97
Polypropylene[f]	..	..	Fair	110	110
Neoprene[g]	3.3	.33	Good	176	176
Neoprene[g]	3.3	..	None	.....	176
Neoprene[g]	..	.33	Good	177	177

[a] Weights are based on 100 g. of polymer in *o*-dichlorobenzene. [b] MPD = N,N′-*m*-phenylenedimaleimide. [c] 5% solution of the polymer. [d] Mol. wt. 25,000 (Union Carbide and Carbon), 5% solution. [e] Hi-fax, 3% solution. [f] Pro-fax, 3% solution. [g] Type W, 6% solution.

Amino-containing Polymers.—Dimaleimides functioned as cross-linking agents for three types of amino-containing polymers; namely gelatin, polyethylenimine and polymers bearing amino end-groups.

(a) **Gelatin.**—In previous work by other investigators polymers of the protein type have been insolubilized by a variety of reagents including formaldehyde, metallic ions, ferricyanide and, more recently, a water-soluble carbodiimide.[6]

Gelatin was converted to insoluble gel by N,N′-ethylenedimaleimide in hot aqueous solution, the gel being formed as a surface film at a moderate rate. In the absence of dimaleimide no gelation was observed. The cross-linking presumably involves the free amino groups present in the lysine, arginine and histidine units of gelatin as illustrated in the structure.



II

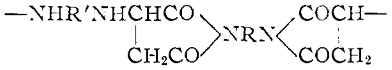
N-Phenylmaleimide and gelatin in aqueous solution produced only a slight turbidity with no gel formation.

(b) **Polyethylenimine.**—Polyethylenimine reacted with dimaleimides, *e.g.*, N,N′-hexamethylenedimaleimide and N,N′-4,4′-biphenylmethylenedimaleimide, to give putty- or crumb-like solids. A filler effect was not responsible for the change in physical state of the polymer since the solid state existed above the melting point of the dimaleimide.

In hot aqueous solution at the ratio of two $-CH_2-CH_2NH-$ units per mole of N,N′-ethylenedimaleimide a resin formed which was precipitated by dioxane. The product probably consists of a three-dimensional network possessing the cross-link structure shown in II.

It should be pointed out that for the various examples of crosslinking with dimaleimides the evidence is least firm in the case of polyethylenimine.

(c) **Polymers with Amino End-groups.**—It has been reported[2] previously that low molecular weight polymers containing amino end-groups can be chain-extended with dimaleimides. The following structure is believed to result from this process.



Cross-linking was facilitated by addition of a triamine, although its presence was not essential.

The proposed modes of reaction involving amino-containing polymers and dimaleimides are supported by the work[7] of Frankel, Liwschitz and Amiel. They found that benzylamine added to the α,β-unsaturated linkage of maleic anhydride in a reaction also accompanied by ring opening.

For such cases of cross-linking, side reactions to be considered are an intramolecular cyclization involving the dimaleimide and two amino groups of a single polymer molecule, and an addition to only one of the unsaturated units of the dimaleimide to form a side-chain.

Urethan Polymer.—Use of N,N′-*m*-phenylenedimaleimide with catalytic amounts of dicumyl peroxide produced a high state of cure with Adiprene C (Table III). Control experiments established that cross-linking resulted from a combined action of the additives. Vulcanizate properties were similar to those obtained with a sulfur–accelerator system or with higher concentrations of dicumyl peroxide alone.

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[4] P. Kovacic and R. W. Hein, THIS JOURNAL, **81**, 1190 (1959).

[5] E. H. Farmer and C. G. Moore, *J. Chem. Soc.*, 131 (1951).

[6] J. C. Sheehan and J. J. Hlavka, THIS JOURNAL, **79**, 4528 (1957).

[7] M. Frankel, Y. Liwschitz and Y. Amiel, *ibid.*, **75**, 330 (1953).

TABLE III

ADIPRENE, N,N′-*m*-PHENYLENEDIMALEIMIDE AND DICUMYL PEROXIDE

Adiprene C, 100 g.; Philblack O, 30 g.; N,N′-*m*-phenylenedimaleimide (MPD), as shown; dicumyl peroxide (DICUP), as shown; cure, 45 min./155°.

MPD, g.	DICUP, g.	M_{200}	M_{300}	T_B	E_B	Res.	Set
..	1.4	1900	2850	3150	310	60	4.1
..	0.3	Undercured					
2.0	.3	1700	2750	3100	310	57	5.1
2.5	.3	2100	..	2700	250	59	4.9
3.0	..	200	250	<800	890	53	8.1
..[a]	..[a]	1100	2250	3650	490	63	5.7

[a] Reference cure[8]: 2,2′-dibenzothiazyl disulfide (4 g.), 2-mercaptobenzothiazole (1 g.), sulfur (0.7 g.), Activator RCD-2098 (0.35 g.)

Since the composition of Adiprene C has not been disclosed other than that it is a urethan rubber,[8] little can be said concerning its mode of cross-linking. Adiprene B is described[9] in the literature as a polymer derived from a diisocyanate and a polyether glycol.

It is interesting that Adiprene C is not insolubilized by N,N′-*m*-phenylenedimaleimide–dicumyl peroxide on heating in *o*-dichlorobenzene.

In all likelihood the reactions of dimaleimides with amino-containing polymers involve ionic mechanisms, whereas those with unsaturated hydrocarbon polymers and polyethylene involve free radical intermediates.

Evidently, dimaleimides possess a desirable versatility as demonstrated by their ability to cross-link polymers of widely differing types. In addition, it might be possible by variation in the structure of the dimaleimide to study the relationship between the nature of the cross-link and vulcanizate properties.

A number of polymers investigated gave no evidence of cross-linking with the dimaleimide–peroxide combination in solution. Certain of these, in addition to Adiprene C, might be cross-linked under other conditions.

Acknowledgment.—Support of this work by the U. S. Military Medical Supply Agency and by the Case Research Fund is acknowledged.

TABLE IV

DIMALEIMIDES AND DIMALEAMIC ACIDS

Starting diamine	Crystn. solvent[a]	M.p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
		Dimaleimides							
m-$NH_2C_6H_4NH_2$	TE(aq.D)	202[b,c]	$C_{14}H_8N_2O_4$	62.69	62.89	3.01	3.40	10.45	9.91
p-$NH_2C_6H_4NH_2$	TE(aq.D)	346–350[c]	$C_{14}H_8N_2O_4$	62.69	63.02	3.01	3.48	10.45	10.18
p,p′-$NH_2C_6H_4C_6H_4NH_2$	Aq.D	340–349[c]	$C_{20}H_{12}N_2O_4$	69.73	69.47	3.51	3.84	8.14	8.04
p,p′-$NH_2C_6H_4CH_2C_6H_4NH_2$	T(E)	158	$C_{21}H_{14}N_2O_4$	70.39	70.64	3.94	4.25	7.82	7.54
$NH_2CH_2CH_2NH_2$	Aq.E	190–192	$C_{10}H_8N_2O_4$	54.55	54.73	3.66	3.78	12.72	12.53
$NH_2(CH_2)_6NH_2$	Aq.M	139–140	$C_{14}H_{16}N_2O_4$	60.86	60.46	5.84	5.53	10.14	9.82
		Dimaleamic acids							
$NH_2CH_2CH_2NH_2$	Aq.E	181–182[c]	$C_{10}H_{12}N_2O_6$	46.88	46.57	4.72	4.76	10.93	10.98
$NH_2(CH_2)_6NH_2$	Aq.M	173–174[c]	$C_{14}H_{20}N_2O_6$	53.84	52.96	6.45	6.25	8.97	8.61

[a] T = toluene, E = ethanol, M = methanol, D = dioxane. [b] Lit.[3] m.p. 198–199°. [c] Sample inserted in bath about 10° below the melting point.

Experimental[10,11]

Materials.—All of the materials used were the highest purity commercial grades available.

Preparation of Dimaleimides.—The method[3] of Searle was followed with modifications. In the last step, a 2.5:1 molar ratio of acetic anhydride to dimaleamic acid was used. Temperature control is more critical for ring-closure of the aliphatic dimaleamic acids than for the aromatic ones. The temperature of the mixture should be taken to the point (about 92°) at which a clear solution results, held in this region until the exothermic reaction subsides and then lowered. The crude form of the aromatic dimaleamic acids was used since purification proved very difficult. After rigorous purification, the dimaleimides were obtained in yields of 5–15% (aromatic ones, pale yellow; aliphatic ones, white). Data for the dimaleimides and dimaleamic acids are given in Table IV.

Gelation Studies.—The general procedure is illustrated by the following example. A mixture of pale crepe (6 g.) and *o*-dichlorobenzene (194 g.) was heated under nitrogen with stirring. At about 65° N,N′-*m*-phenylenedimaleimide (0.3 g.) and dicumyl peroxide (0.03 g.) were added. The pale crepe dissolved at about 100° producing a relatively thin solution. At 125° the solution began to thicken and at 128° semi-transparent gel separated making stirring difficult since the gel adhered to the stirrer. The mixture was heated for 5 minutes at 128–131° without a change in gel consistency. In most cases, 1.5-2 hours was taken to reach the maximum temperature.

The preceding example represents a "good" gel. A "fair" gel was less viscous–when stirring was stopped the gel fell from the stirrer and took the shape of the vessel. A "slight" gelation occurred when the solution increased markedly in viscosity but no gel separation was observed.

Gelatin and N,N′-Ethylenedimaleimide.—The following experiments were performed with gelatin[12] (5 g.), N,N′-ethylenedimaleimide (EDM, g.) and water (H_2O, ml.): EDM (0.5), H_2O (75); EDM (0.5), H_2O (125); EDM (1), H_2O (125); EDM (1.5), H_2O (125). The mixtures were heated for 1–2 hours on a steam-bath in lightly stoppered flasks. In all cases, gel formed slowly, appearing on the surface within 5–15 minutes, and continued to form at a slow rate. An increase in the volume of solvent increased the time for gel separation. The controls, containing no EDM, yielded no gel. After the reaction mixture from EDM, 0.5 g., and H_2O, 75 ml., was heated for 2.5 hours, 200 ml. of water was added and the mixture was allowed to stand overnight. Gel was still present and no crystalline solid separated. After 1.5 hours on a steam-bath the gel remained undissolved.

Gelatin and N-Phenylmaleimide.—A solution of gelatin (5 g.) and N-phenylmaleimide (0.5 g.) in boiling water (100 ml.) was heated on a steam-bath for 2.5 hours. The solution became turbid within 5 minutes and at the end a trace amount of tan precipitate was present. No solid was ob-

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(8) Development Products Report No. 4 (1957), E. I. du Pont de Nemours and Co.

(9) F. B. Hill, C. A. Young, J. A. Nelson and R. G. Arnold, *Ind. Eng. Chem.*, **48**, 927 (1956).

(10) Mr. Ralph Hodous assisted in the experimental work.

(11) Analyses were performed by Weiler and Strauss, Oxford, England. All melting points are corrected.

(12) 175 Bloom, 10% water; General Biochemicals, Inc.

tained from filtration of the cooled solution and no gel formation was observed.

Polyethylenimine and Dimaleimides. (A) With Solvent.—A solution of N,N′-ethylenedimaleimide (0.5 g.) in 25 ml. of boiling water was poured slowly with stirring into a hot solution of polyethylenimine (0.4 g.) (50% aqueous solution, Hansborg and Co.) in 5 ml. of water, and then heated on the hot-plate for 5 minutes. The reaction mixture was cloudy with a trace of precipitate present and was unchanged in appearance at room temperature. Addition of 250 ml. of dioxane caused the separation of a white, flocculent solid which was filtered, washed with dioxane (20 ml.) and then dried at 130°, wt. 0.6 g., light brown, resinous solid.

(B) Without Solvent.—The following experiments were performed with 10 g. of polyethylenimine and 1.4 g. of dimaleimide with manual stirring.

Dimaleimide	Temp., °C.	Time, min.	Product description
N,N′-Hexamethylene-	100–105[a]	5	Putty
N,N′-4,4′-Biphenylmethylene-	160–165	10	Crumb
N,N′-*m*-Phenylene-	130–140	5	Putty

[a] A small amount was taken and heated to 150° with retention of its solid nature.

The products had a solid consistency at the elevated temperatures as well as at room temperature.

Polyethylenimine and N-Phenylmaleimide.—A mixture of polyethylenimine (10 g.) and N-phenylmaleimide (1.4 g.) was heated with manual stirring to 103° in 10 minutes. The product was a putty-like solid at the elevated temperatures and at room temperature.

Polymers giving no gelation with N,N′-*m*-phenylenedimaleimide–dicumyl peroxide: polymethylmethacrylate, polystyrene (F-20), polyvinyl alcohol (Elvanol 70–05), polyvinylpyrrolidone (Type NP), polyvinyl chloride (Geon 121, Marvinol VR-10), polyvinyl butyral (Filtered No. 2), polyisobutylene, Adiprene C, polybutadiene (Butarez No. 15), Hypalon S_2 (chlorosulfonated polyethylene), Thiokol (Type ST) (see Table V), Thiokol (Type LF32), polydimethylsiloxane (Dow Corning 200 Fluid, 1000 cs.), polyformaldehyde (Delrin), methyl cellulose (Methocel).

Recipe (by wt.): polymer (100), N,N′-*m*-phenylenedimaleimide (4) and dicumyl peroxide (0.4). The solvent was *o*-dichlorobenzene except for polyformaldehyde (dimethylformamide) and methyl cellulose (butyl Cellosolve). A 5% solution of polymer was used except for methyl cellulose (3%), polydimethylsiloxane, polybutadiene and Thiokol Type LF32 (20%). The solution was heated to a maximum temperature of 170–180° except for polyformaldehyde (152°).

TABLE V

THIOKOL, N,N′-*m*-PHENYLENEDIMALEIMIDE AND DICUMYL PEROXIDE

Thiokol ST, 100 g.; SRF Black, 40 g.; N,N′-*m*-phenylenedimaleimide (MPD), as shown; dicumyl peroxide (DICUP) as shown; cure 30 min./155°

MPD, g.	DICUP, g.	M_{200}	T_B	E_B	Res.	Set
..	3.0	200	300	290	28.4	28.1
3.0	0.3	400	450	210	33.1	19.8
..[a]	..[a]	925	1200	270	..	45

[a] Reference cure[13]: SRF Black (60), stearic acid (1), zinc peroxide (6).

Testing Procedure.—A Scott tensile tester, model XL, was used with dumbbell specimens 0.075 in. thick. Resilience was determined at room temperature with the Yerzley oscillograph, and compression set by ASTM method B: pellet samples were depressed 30% for 22 hours at 70°. Set, resilience and elongation are reported as percentages; modulus and tensile data are in lb./sq. in.

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(13) Bulletin, "Thiokol Synthetic Rubber, Type ST," Thiokol Chemical Corp., Aug., 1955.

CLEVELAND 6, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, CASE INSTITUTE OF TECHNOLOGY]

Cross-linking of Unsaturated Polymers with Dimaleimides[1]

BY PETER KOVACIC AND RICHARD W. HEIN

RECEIVED AUGUST 8, 1958

A study was made of the cross-linking of unsaturated polymers with dimaleimides representative of both the aliphatic and aromatic series. In the presence of catalytic amounts of dicumyl peroxide, dimaleimides functioned as highly effective cross-linking agents for natural rubber and GR-S. Comparatively little cross-linking occurred in the absence of peroxide under thermal conditions. With peroxide as a promoter, monomaleimides and dimaleamic acids also cross-linked natural rubber, but to a lesser extent than did the dimaleimides. The chemistry of the cross-linking process is discussed, and correlations are drawn between the structure of the dimaleimide and vulcanizate properties.

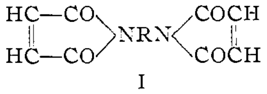
Introduction

The main objectives of this work were to: (a) investigate the cross-linking ability of dimaleimides with unsaturated polymers, (b) study the chemistry of the reactions involved and (c) correlate the structure of the dimaleimide with vulcanizate properties.

Dimaleimides represent a recent addition to the group of compounds which cross-link polymers. They possess a desirable versatility in their ability to cross-link polymers of widely differing types.[2,3]

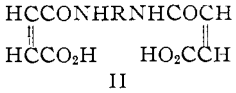
Results

The dimaleimides (I), dimaleamic acids (II) and N-phenylmaleimide were synthesized according to the method of Searle[4] and are described in a preceding publication.[2]



$$\begin{array}{l} HC{-}CO \\ \| \\ HC{-}CO \end{array}\!\!>NRN<\!\!\begin{array}{l} COCH \\ \quad\ \| \\ COCH \end{array}$$

I



$$\begin{array}{l} HCCONHRNHCOCH \\ \| \qquad\qquad\qquad\qquad \| \\ HCCO_2H \qquad HO_2CCH \end{array}$$

II

N,N′-*m*-Phenylenedimaleimide was able to vulcanize natural rubber in the absence of added catalyst, but the degree of cross-linking was relatively low (Table I). At the high temperatures used (184°), thermal degradation of the rubber

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(1) Paper II in the series "New Cross-linking Agents for Polymers." This paper was presented in part at the 134th Meeting of the American Chemical Society in Chicago, Ill., September, 1958, and is an abstract of a portion of the M.S. thesis of R. W. Hein, Case Institute of Technology, 1958.

(2) P. Kovacic and R. W. Hein, THIS JOURNAL, **81**, 1187 (1959).

(3) P. Kovacic, U. S. Patent 2,818,405 (1957); *C. A.*, **52**, 5018 (1958).

(4) N. E. Searle, U. S. Patent 2,444,536 (1948); *C. A.*, **42**, 7340 (1948); H. W. Arnold and N. E. Searle, U. S. Patent 2,462,835 (1949); *C. A.*, **43**, 4121 (1949).