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

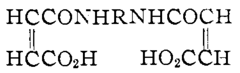
The main objectives of this work were to: (a) investigate the cross-linking ability of dimaleimides with unsaturated polymers, (b) study the chemistry of the reactions involved and (c) correlate the structure of the dimaleimide with vulcanizate properties.

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]

I



$$\begin{array}{ccc} HCCONHRNHCOCH & & \\ \| & & \| \\ HCCO_2H & & HO_2CCH \end{array}$$

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 11 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**, 4421 (1949).

TABLE I

NATURAL RUBBER AND N,N′-*m*-PHENYLENEDIMALEIMIDE: THERMAL EFFECTS

Pale crepe. N,N′-*m*-phenylenediamaleimide (MPD), wt.g/100 g. as shown

MPD, g.	Cure, min./°C.	M_{500}	M_{700}	T_B	E_B	Res.	Set
1	30/184	100	150	<800	850	70	8.3
2	30/184	150	..	<800	650	76	5.6
3	30/184	300	1150	1500	750	79	4.8
4	30/184	350	1500	1700	725	80	4.3
3	45/170	200	950	1000	700	77	4.4
3	45/155	200	600	1150	800	72	8.4

would contribute to a certain extent to the comparatively poor mechanical properties.

Addition of a small amount of dicumyl peroxide resulted in a pronounced promoting effect. With 3% of the dimaleimide and 0.3% of peroxide, excellent cures were obtained on heating at 155° for 45 minutes (Table II). As is seen from Table III, there was a progressive deterioration of vulcanizate properties, especially modulus, with decrease in peroxide concentration below 0.3%. With dicumyl peroxide alone, the catalytic quantities used produced only a very slight degree of vulcanization. All of the other compounds investigated as promoters, including benzoyl peroxide and tetramethylthiuram disulfide, exhibited little or no activity (Table IV).

TABLE II

NATURAL RUBBER, DIMALEIMIDES AND DICUMYL PEROXIDE

Pale crepe, 100 g.; N,N′-(R) dimaleimide, as shown; dicumyl peroxide (DICUP), as shown; cure, 45 min./155°

Dimaleimide, R =	Wt., g.	DICUP, g.	M_{300}	M_{500}	T_B	E_B	Res.	Set
m-Phenylene	3.0	..	100	200	1150	800	72	8.4
m-Phenylene	3.0	.3	300	1700	1950	525	85	0.8
p-Phenylene	3.0	..	50	50	<800	750	67	14.5
p-Phenylene	3.0	.3	450	2100	2100	500	86	1.5
p,p′-Diphenylene	3.9	..	50	75	<800	675	66	16.6
p,p′-Diphenylene	3.9	.3	300	1700	2150	540	81	1.2
p,p′-Diphenyl-	4.0	..	50	150	<800	725	70	7.9
methylene	4.0	.3	300	..	1100	475	81	0.8
p,p′-Diphenyl-methylene	3.4	.3	200	1000	1200	510	82	0.9
Ethylene	2.5	..	50	150	1100	890	70	7.9
Ethylene	2.5	.3	250	1450	1550	510	84	0.7
Hexamethyl-	3.1	..	50	150	1000	800	73	5.3
ene	3.1	.3	250	..	900	480	84	1.1
None	..	.3	100	150	1200	1000	69	6.3

TABLE III

NATURAL RUBBER, N,N′-*m*-PHENYLENEDIMALEIMIDE AND DICUMYL PEROXIDE

Pale crepe, 100 g.; N,N′-*m*-phenylenedimaleimide, 3 g.; dicumyl peroxide (DICUP) promoter, as shown

DICUP, g.	Cure min./155°	M_{500}	T_B	E_B	Res.	Set
0.07	20	350	1600	720	76	4.9
.07	45	700	2100	670	81	2.1
.14	20	600	1800	670	81	3.6
.14	45	1000	1900	650	82	1.8
.3	10	750	1900	660	80	3.1
.3	20	1050	1900	580	82	2.2
.3	45	1700	1950	525	85	0.8

TABLE IV

NATURAL RUBBER, N,N′-*m*-PHENYLENEDIMALEIMIDE AND PROMOTERS

Pale crepe, 100 g.; N,N′-*m*-Phenylenedimaleimide, 3 g.; promoter, as shown; cure, 45 min./155°

Promoter	Wt., g.	M_{500}	T_B	E_B	Res.	Set
Dicumyl peroxide	0.3	1700	1950	525	85	0.8
Benzoyl peroxide	.3	..	200	410	72	6.3
2,2′-Dibenzothiazyl disulfide	.3	100	<800	825	67	11.9
Polyac[a]	1.1	250	1700	750	75	8.3
Cure: 30 min./184°						
Dicumyl peroxide	0.3	..	<800	250	85	0.6
Dicumyl peroxide	.14	1000	1850	600	81	2.5
Benzoyl peroxide	.3	700	1100	690	73	4.0
Di-*t*-butyl disulfide	.4	200	1200	800	73	5.8
Tetramethylthiuram disulfide	.4	200	1000	725	72	5.4

[a] Poly-*p*-dinitrosobenzene diluted with an inert ingredient.

Studies were made with dimaleimides representative of both the aliphatic and aromatic series, namely those prepared from *m*- and *p*-phenylenediamine, *p,p*′-diaminodiphenyl, *p,p*′-diaminodiphenylmethane, ethylenediamine and hexamethylenediamine. All produced a high degree of cross-linking with natural rubber in the presence of catalytic amounts of dicumyl peroxide (Table II).

It was found that common fillers such as carbon black, titanium dioxide and zinc oxide had no noticeable adverse effect upon the cross-linking by dimaleimide–dicumyl peroxide (Table V).

TABLE V

NATURAL RUBBER, N,N′-*m*-PHENYLENEDIMALEIMIDE AND FILLERS

Pale crepe, 100 g.; zinc oxide, 5 g.; N,N′-*m*-phenylenedimaleimide, 3 g.; dicumyl peroxide (DICUP), as shown; filler, as shown; cure, 45 min./155°

Filler	Wt., g.	DICUP, g.	M_{300}	M_{500}	T_B	E_B	Res.	Set
ZnO	[a]	..	100	300	1600	760	76	10.8
ZnO	[a]	0.07	200	1000	1600	590	82	3.3
ZnO	[a]	.14	300	1350	1750	510	85	2.4
SRF black	40	..	500	1400	1600	520	60	15.5
SRF black	40	.07	1300	..	3000	490	72	7.2
SRF black	40	.14	1700	..	2500	380	77	3.8
TiO_2	40	..	200	800	1500	630	73	10.0
TiO_2	40	.07	500	1700	2000	550	80	4.2
TiO_2	40	.14	600	..	1600	450	84	3.0

[a] As shown in the recipe.

In Table VI, data show that this vulcanizing system also is highly effective with GR-S.

TABLE VI

GR-S, N,N′-*m*-PHENYLENEDIMALEIMIDE AND DICUMYL PEROXIDE

GR-S-1500, 100 g.; N,N′-*m*-phenylenedimaleimide, 3 g.; dicumyl peroxide (DICUP), as shown; cure, 45 min./155°

DICUP, g.	M_{300}	M_{500}	T_B	E_B	Res.	Set
..	75	100	<800	1200	54	19.1
0.07	200	..	<800	350	65	3.9
.14	..	..	<800	200	71	2.8
.3	..	..	<800	150	77	0.5
.3[a]	100	150	<800	700	62	5.9

[a] No N,N′-*m*-phenylenedimaleimide.

These compounding studies with natural rubber and GR-S fully confirm the results[2] obtained from gelation studies in solution. Furthermore, the vulcanizates are comparable in many of their mechanical properties to those obtained with sulfur or dicumyl peroxide (Tables VII and VIII).

TABLE VII

NATURAL RUBBER AND SULFUR–ACCELERATOR

Pale crepe, 100 g.; N-phenyl-2-naphthylamine, 2 g.; stearic acid, 1 g.; zinc oxide, 5 g.; sulfur, 3 g.; 2-mercaptobenzothiazole (2-MBT), as shown; cure, 40 min./135°

2-MBT, wt., g.	M_{600}	T_B	E_B	Res.	Set
4	660	3500	740	93	12
6	720	3500	740	93	12

TABLE VIII

NATURAL RUBBER AND DICUMYL PEROXIDE

Pale crepe, 100 g.; dicumyl peroxide (DICUP), as shown; cure, 45 min./155°

DICUP, g.	M_{300}	M_{600}	T_B	E_B	Res.	Set
2.25	250	1100	1300	510	87	0.1
2.50	300	..	1100	470	87	.4
3.00	400	..	900	440	88	.4

A monomaleimide, N-phenylmaleimide, also vulcanized natural rubber (Table IX) but was much less effective than the dimaleimides. The decreased effectiveness of the monomaleimide was illustrated also by the lack of gelation observed with this reagent and natural rubber in solution in the presence of dicumyl peroxide (Table XI). A similar situation prevailed with dimaleamic acids (Tables X and XI).

TABLE IX

NATURAL RUBBER, N-PHENYLMALEIMIDE AND DICUMYL PEROXIDE

Pale crepe, 100 g.; N-phenylmaleimide, as shown; dicumyl peroxide, 0.3 g.; cure, 45 min./155°

N-Phenylmaleimide, g.	M_{600}	M_{700}	T_B	E_B	Res.	Set
3.9[a]	100	125	650	1100	67	12.1
5.9	700	..	1800	610	81	1.6
3.9	300	1400	1500	710	78	2.4
2.0	200	800	1300	790	77	2.0

[a] No dicumyl peroxide.

TABLE X

NATURAL RUBBER, DIMALEAMIC ACIDS AND DICUMYL PEROXIDE

Pale crepe, 100 g.; N,N'-(R)dimaleamic acid, as shown; dicumyl peroxide, 0.3 g.; cure, 45 min./155°

Dimaleamic acid, R =	Wt., g.	M_{600}	M_{700}	T_B	E_B	Res.	Set
m-Phenylene	3.4	500	2000	2300	720	83	4.0
Ethylene	2.9	300	700	1600	790	73	3.2

Discussion

The Chemistry of Cross-linking.—The experimental results indicate that at least two types of reactions, both of which are free radical in nature, are involved in the cross-linking of natural rubber with dimaleimides. The following evidence suggests that a free radical chain mechanism is operative: (a) dimaleimides alone can cross-link natural rubber at high temperatures but only to a relatively slight extent, (b) addition of a catalytic amount of peroxide to this system greatly increases the degree of cross-linking.

TABLE XI

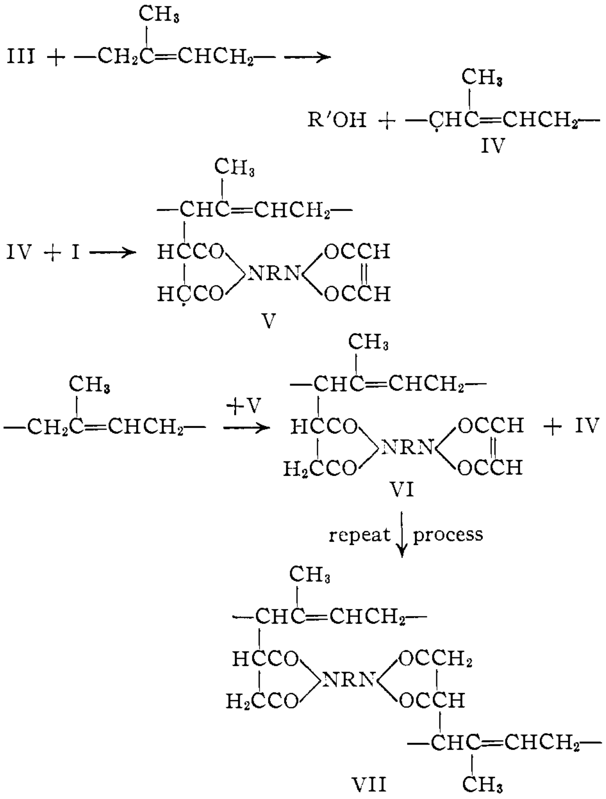
ATTEMPTED GELATION OF NATURAL RUBBER WITH N-PHENYLMALEIMIDE AND N,N'-*m*-PHENYLENEDIMALEAMIC ACID[a]

Cross-linking agent, g.	Extent of gelation[b]
N-Phenylmaleimide	
6.4[c]	None
9.7	None
12.9	None
N,N'-*m*-Phenylenedimaleamic acid	
5.7	None

[a] Weights are based on 100 g. of pale crepe as a 3% solution in *o*-dichlorobenzene containing 0.5 g. of dicumyl peroxide. The solution was heated to about 175°. [b] By visual observation. [c] Same result in the absence of dicumyl peroxide.

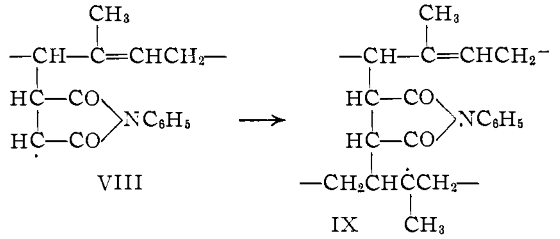
The illustrated reaction sequence is proposed as the principal mode of cross-linking by dimaleimides in the presence of peroxide promoter.

$$R'OOR' \longrightarrow 2R'O\cdot \quad \text{III}$$



The initiating free radical III abstracts an allylic α-hydrogen atom from the natural rubber, represented by a single isoprene unit, to give a free radical IV on the polymer chain. Then IV attacks a dimaleimide molecule to give the new free radical V. After a chain-transfer reaction to give VI, the other maleimide unit of VI proceeds through an analogous sequence, which results in a cross-link as shown in VII. Actually, the chain-transfer reaction could proceed by an intramolecular abstraction of hydrogen by V or by attack on a peroxide molecule (induced decomposition). Also, the termination reaction might occur in a number of ways: disproportionation or combination of any two of the radical intermediates. Some of these terminations would also result in cross-links.

The second type of cross-linking reaction is evidenced by experiments with N-phenylmaleimide. This monomaleimide does crosslink natural rubber in the presence of peroxide, but to a much smaller extent than do the dimaleimides. This suggests that processes of the following type may represent the primary cross-linking reaction for monomaleimides, but a secondary one for dimaleimides.

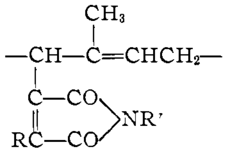

VIII

IX

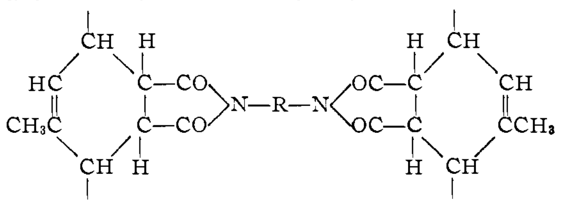
In this type of cross-linking, VIII is first formed and then reacts with the double bond of another polymer chain. The new radical IX may continue the propagation reaction or effect a chain transfer. Termination would result from combination with another free radical or from disproportionation. Termination arising from the union of two VIII units or from VIII and IV would also produce chain-links. Furthermore, the free radical VIII may undergo an intramolecular addition reaction with a double bond.

The low state of cure with N-phenylmaleimide points to a predominance of a chain-transfer reaction analogous to the conversion of V to VI. This does not result in a cross-link with a monomaleimide, but does with a dimaleimide.

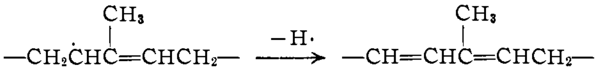
Consideration should also be given to the possible presence of structures of type X on the basis of work[5] done by Rondestvedt and Vogl. They studied the reactions of maleimides with diazonium salts in the presence of cupric chloride and isolated α-aryl- and α,α'-diarylmaleimides.


X, R = H or polymer chain

An additional possible source of cross-links involving dimaleimides is that from a Diels–Alder reaction which leads to the cross-link structure



Since a 1,3-diene is required for formation of the adduct, it is clear that the normal units of natural rubber with a 1,5-diene structure could not participate. However, the requisite conjugated diene might be formed as



$$-CH_2\dot{C}H\overset{CH_3}{\overset{|}{C}}=CHCH_2- \xrightarrow{-H\cdot} -CH=CH\overset{CH_3}{\overset{|}{C}}=CHCH_2-$$

Another cross-linking reaction which may occur in these systems is that which results in a chain-to-chain cross-link as is postulated[6] for peroxide vulcanization. Control experiments with catalytic amounts of dicumyl peroxide demonstrate conclusively that cross-linking of this type is of negligible importance.

Experiments with dimaleamic acids representative of both the aromatic and aliphatic series show that cross-linking is also accomplished, but to only a slight degree. Steric factors or polar effects associated with the carboxyl group may be responsible for the decreased facility for reaction in comparison with the dimaleimides.

In addition to the evidence already cited, there is a considerable amount of experimental work reported in the literature which supports our theoretical interpretations. Examples analogous to the proposed cross-linking reactions are found in simpler chemical systems involving maleimides, maleic anhydride, maleic esters and azodicarboxylates.

Delalande[7] has made an excellent study of the reaction of N-methylmaleimide with natural rubber. Under thermal conditions (160-200°), no gelation occurred and only a small fraction of the olefinic units in the rubber were saturated. The maleimide was chemically bound to the polymer presumably at the allylic positions. With *p*-bromobenzoyl peroxide as a promoter, soluble products were also formed provided the concentration of the cross-linking agents was low. The theoretical interpretations of our work are similar in some respects to those of Delalande who proposed initiation of a chain reaction by peroxide, propagation with the maleimide and several possible termination reactions.

Much study has been devoted to the reaction of maleic anhydride with olefins. Maleic anhydride can be made to combine with natural rubber at temperatures in the vicinity of 200°, and at 100° in the presence of peroxide.[8] In a less complex system, Alder and co-workers found that propylene combined with maleic anhydride to give allylsuccinic anhydride.[9] Bickford and co-workers demonstrated[10] an analogous reaction for aralkyls with peroxide as a promoter.

Similar type reactions can occur[8b] between maleic esters and olefins such as cyclohexene or natural rubber.

The currently accepted mechanism for reactions of this general category is a free radical chain process involving the allylic positions of the olefin with addition across the α,β-unsaturated linkage being the end result.

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[5] C. S. Rondestvedt, Jr., and O. Vogl, THIS JOURNAL, **77**, 2313 (1955).

[6] E. H. Farmer and C. G. Moore, *J. Chem. Soc.*, 142 (1951).

[7] A. Delalande, *Rev. gen. caoutchouc*, **26**, 426 (1949); *Rubber Chem. and Tech.*, **25**, 74 (1952); A. Delalande, *Bull. soc. chim.*, 773 (1951); *Rubber Chem. and Tech.*, **25**, 275 (1952).

[8] (a) R. G. R. Bacon and E. H. Farmer, *Proc. Rubber Tech. Conf.*, 256 (1938); *Rubber Chem. and Tech.*, **12**, 200 (1939); (b) E. H. Farmer, *Trans. Faraday Soc.*, **38**, 340 (1942).

[9] K. Alder, F. Pascher and A. Schmitz, *Ber.*, **76**, 27 (1943).

[10] W. G. Bickford, G. S. Fisher, F. G. Dollear and C. E. Swift, *J. Am. Oil Chem. Soc.*, **25**, 251 (1948).

Ethyl azodicarboxylate has been shown to form adducts with natural rubber[9] and with 2-methyl-2-butene.[11] With disazodicarboxylates[12] natural and synthetic rubbers reacted rapidly at relatively low temperatures to produce good vulcanizates without the aid of other ingredients.

The previous discussion concerning natural rubber can also be applied with adaptations to the cross-linking of GR-S taking into account additional factors associated with the polymer structure such as units derived from 1,2-polymerization and the labile *t*-hydrogens in the styrene units.

Relationship between Dimaleimide Structure and Vulcanizate Properties.—Both aliphatic and aromatic dimaleimides gave similar vulcanizates with natural rubber in relation to the properties of resilience and compression set, whereas the aliphatic ones, on a molar basis, produced slightly lower modulus values. The most striking difference is that those dimaleimides derived from diamines possessing any degree of aliphatic hydrocarbon character yielded vulcanizates with particularly poor tensile strength. The underlying cause may reside in differences in flexibility of the crosslink structure, or in chemical participation of the methylene groups during vulcanization so as to affect tensile strength adversely.

Experimental[13]

Materials.—The dimaleimides, dimaleamic acids and N-phenylmaleimide were prepared as previously described.[2,4] Other materials used were the highest purity commercial grades available.

Testing Procedure.—The procedure followed is reported elsewhere.[2]

Acknowledgment.—We wish to acknowledge the support of this work by the U. S. Military Medical Supply Agency.

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(11) N. Rabjohn, THIS JOURNAL, **70**, 1181 (1948).

(12) P. J. Flory, N. Rabjohn and M. C. Shaffer, *J. Polymer Sci.*, **4**, 225 (1949); **4**, 435 (1949).

(13) The compounding, curing and testing were done by Mr. Ralph Hodous.

CLEVELAND 6, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

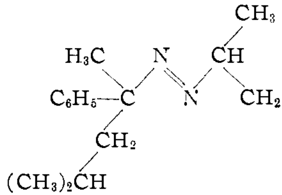
Azo Compounds. XXVIII.[1] A Decomposition Study of α,α-Methylisobutylbenzylazo-2-(4-methylpentane)

BY C. G. OVERBERGER AND A. V. DIGIULIO[2]

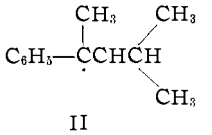
RECEIVED SEPTEMBER 19, 1958

The decomposition of I in xylene gave a mixture of products resulting from combination and disproportionation reactions of α,α-methylisobutylbenzyl radical (II) and the methylisobutylcarbinyl radical (III), as well as products derived from solvent interaction with these radicals. The lack of formation of any coupled product from the radical $(C_6H_5)C(CH_3)(CH_2CH)(CH_3)_2)$ and the low yield of unsymmetrical coupled product may be due to an unfavorable steric factor.

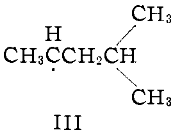
I. Products.—A 30% and a 12% solution of the azo compound I was decomposed in xylene at 110° yielding a mixture of the same products, with slightly varying yields of the individual products. The mixture was shown to consist of product principally derived from the α,α-methylisobutylbenzyl (II) and the methylisobutylcarbinyl (III) radicals as well as product which also incorporated solvent molecules.



I



II



III

The products were initially separated into four main fractions consisting of mixtures as shown in Table I (see Experimental section) by two fractionations. The initial separation into main fractions, Table I, indicated a total yield of products of 105 and 109%, respectively, which indicated that solvent radicals were being generated and were interacting with the radicals generated by the decomposition of the azo compound or possibly with other solvent radicals. The initial separation in both decompositions yielded approximately 72% of product, respectively, derived solely from radicals derived from the azo compound. The yield of product derived from the solvent and the azo radicals totalled approximately 32 and 35%, respectively.

The initial fraction consisted chiefly of 2-methylpentane and the two possible methylpentenes, derived from radical III. The infrared spectrum indicated the presence of olefin. Hydrogenation of this fraction indicated the presence of ~4.3% of the olefins in the decomposition of a 12% solution and ~15% olefin in the decomposition of a 30% solution. The refractive index and infrared spectrum of the hydrogenated product were identical with those of a pure commercial sample of 2-methylpentane, indicating that the above-mentioned isomers were the only three possible constituents of this fraction. The low olefin content of

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(1) This is the 28th in a series of papers concerned with the preparation and decomposition of azo compounds. For the previous paper in this series, see C. G. Overberger and A. V. DiGiulio, THIS JOURNAL, **80**, 6562 (1958).

(2) This paper comprises a portion of a thesis presented by A. V. DiGiulio in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.