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Chain Scission in the Oxidation of Hevea. II

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Oxidation of natural rubber in latex yields two molecules of carbon dioxide, one of formic acid and one of acetic acid for each rupture of the hydrocarbon chain. The yields of these products can be interpreted readily by reference to the structure of the primary oxidation products of 1,5-diolefins established by Bolland and Hughes.[4]

Introduction

Establishment of the structure of the product formed from cyclohexene by reaction with oxygen[1] initiated a period of increasingly intensive investigation of the interaction of olefins with molecular oxygen which has now reached the stage where it has been described[2] as "one of the most thoroughly understood chemical processes." One general reaction scheme, modified in detail to account for variations in substrate structure, explains the observed features of hydrocarbon autoöxidation in a very satisfactory manner: oxidation of all compounds having the necessary hydrogen adjacent to the (isolated) unsaturation leads to an α-hydroperoxide as primary product.

The subsequent fate, on continued oxidation, of the peroxide formed initially is less thoroughly understood, except for a few relatively simple compounds whose hydroperoxides decompose smoothly by clear reaction paths.[3] The sequence of steps leading to scission of carbon to carbon bonds, of special technological importance in the oxidation of rubber, has remained obscure. For this hydrocarbon, in fact, the considerable experimental difficulties encountered have prevented a direct demonstration of the nature of its initial oxidation product, although the work of Bolland[4] with model compounds leaves little doubt as to its structure.

Further progress in the understanding of this reaction now requires a knowledge of the identity and relative amounts of the products formed when the peroxide decomposes. It has been known for over forty years that volatile products are associated with the oxidation of rubber,[5] being evolved from the beginning of the reaction. Water, carbon dioxide[6] and formic acid[7] have been identified among these. In the earliest work volatile materials were usually dismissed as resulting from minor side reactions or from oxidation of non-rubber constituents, although Dawson and Porritt obtained an estimate of the molecular weight of balata, based on the yield of formic acid obtained by oxidizing it, which was nearly of the right order of magnitude. More recently, volatile compounds have been recognized as real products of the oxidation reaction, although they have not been quantitatively correlated with hydrocarbon degradation: the yields of water and carbon dioxide, for example, were characterized by Farmer and Sundralingham[8] as "small but not negligible."

It has been known for some time that oxidation of latex at low temperature results in the formation of acid.[9] When this was reinvestigated at higher temperatures to obtain reasonable rates of oxidation, the yields of acid were found to be surprisingly high. The results reported here were obtained by further study of this phenomenon.

Although it is possible to measure volatile products of the oxidation of solid rubber or of rubber in solution quantitatively, some of the experimental difficulties can be avoided by carrying out the reaction in latex: the rubber is highly concentrated, yet finely dispersed, so that large samples may be used to obtain adequate yields of oxidation products, without the intrusion of oxygen diffusion effects, and the latex remains stable over a wide range of extents of oxidation so that handling the oxidized rubber is not a problem.

Rigorous purification is not required to obtain reproducible results with latex. The rate of oxidation is constant[9] and much higher than the initial rate of oxidation of dry rubber from the same latex. It is apparently determined by traces of metals, particularly copper, the rate-controlling step involving transfer of metal ions between the two phases. Experiments not reported here have shown the efficiency of scission by oxygen and the yields of volatile products are not affected by changes in copper concentration.

Experimental

The latex used in this work was a commercial creamed latex (United States Rubber Co.), preserved with ammonia, which contained 67 to 68.5% total solids in the samples used.

Oxidation experiments were made with a simple apparatus in which reaction cells consisting of 200-ml. round-bottom flasks were connected to a reservoir of oxygen at the reaction temperature (90°) and through flexible capillary connections to mercury manometers at room temperature. The flasks were mounted on a "Wrist-Action" shaker (Burrell Technical Supply Co.) oscillating at about 240 cycles per minute. Frothing of the latex provides intimate mixing of gas and liquid, so that the extremely vigorous agitation required for oxidation of pure organic liquids[10] was not found necessary here.

Oxidations were carried out at a total pressure of about 1.8 atmospheres, the amount of oxygen consumed being calculated from the pressure drop in the cells. This arrangement, although capable of less precision than measurements at constant pressure, is considerably more convenient experimentally and yields rates of oxidation reproducible within less than 5%. The rates observed were independent

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[1] R. Criegee, *Ann.*, **522**, 75 (1936); R. Criegee, H. Pilz and H. Flygare, *Ber.*, **72B**, 1799 (1939).

[2] L. Bateman, *Quart. Revs.* (*London*), **8**, 147 (1954).

[3] A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y.

[4] J. L. Bolland and H. Hughes, *J. Chem. Soc.*, 492 (1949).

[5] S. J. Peachey, *J. Soc. Chem. Ind.* (*London*), **31**, 1103 (1912).

[6] S. J. Peachey and M. Leon, *ibid.*, **37**, 55 (1918); B. Mead and J. C. Pope, *India Rubber World*, **73**, 326 (1926).

[7] T. R. Dawson and B. D. Porritt, *Trans. Inst. Rubber Ind.*, **2**, 345 (1927).

[8] E. H. Farmer and A. Sundralingham, *J. Chem. Soc.*, 125 (1943).

[9] J. McGavack and E. M. Bevilacqua, *Ind. Eng. Chem.*, **43**, 475 (1951).

[10] J. L. Bolland and H. R. Cooper, *Proc. Roy. Soc.* (*London*), **225A**, 405 (1954).

of oxygen pressure over a wide range and became erratic only when substantial changes in the latex had occurred.

After a sample had absorbed the desired amount of oxygen it was removed from the bath and cooled rapidly to room temperature. Samples of rubber for viscosity determination were obtained by drying aliquots at room temperature. Further oxidation during the drying process was negligible. Viscosities were determined in chloroform solution in Ostwald viscometers and molecular weights calculated from the relation of Carter, Scott and Magat,[11] applying a correction for the 10% higher intrinsic viscosity in chloroform.

Total "titrable acids" were determined by potentiometric titration of an aliquot of the latex with 0.1 *N* NaOH to *p*H 11.2. (This is a measure of the sum of ammonium ion and bicarbonate.) Carbon dioxide was determined by passing a stream of CO_2-free air through a second aliquot, stabilized with Emulphor ON (General Dyestuff Corporation) and made acid with phosphoric acid, collecting it in Ascarite, and weighing. Volatile acid other than CO_2 was determined essentially by the micro method of Philpott and Sekar,[12] using sulfuric acid to coagulate the latex.

The yields of total titrable acid, carbon dioxide and volatile acid from a series of oxidations are plotted in Fig. 1. In order to determine if all titrable acid was accounted for, the amounts of alkali required to titrate the carbon dioxide formed were calculated (Table I) and plotted against the actual titer. A line through these points had a slope of 0.75. Since the volatile acid is very close to one-fourth the total titer (dashed line of Fig. 1), no other acid was formed, within the experimental error.

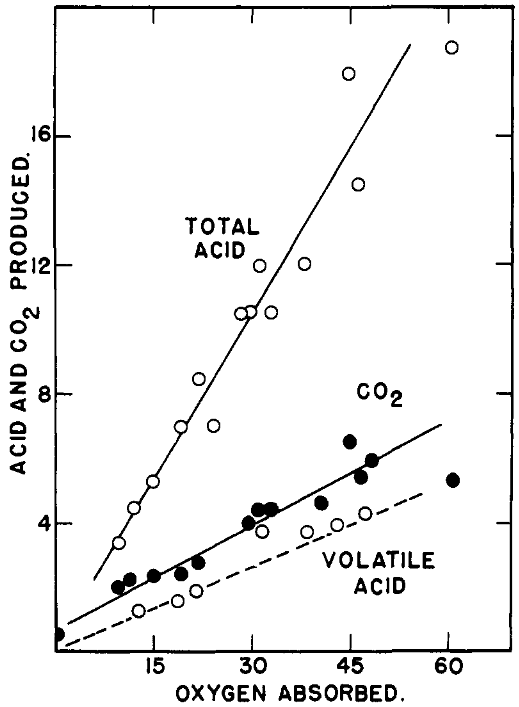

Fig. 1.—Acid and CO_2 produced as a function of oxygen consumed: acids in meq./100 g. latex solids, carbon dioxide and oxygen in mmoles/100 g.

TABLE I

TOTAL ACID AND CARBON DIOXIDE PRODUCED

Oxygen[a] absorbed	Final *p*H	NaOH[a] titer	CO_2[a] found	CO_2 titer[a] calcd.
0	10.00	11.9	1.31	..
0[b]	10.08	11.0	1.06	..
9.9	10.12	15.3	3.26	3.3
12.0	9.90	16.4	3.49	3.8
15.0	9.72	17.2	3.62	4.2
19.0	9.67	18.9	3.66	4.4
22.0	9.48	20.4	4.01	5.2
24.1	9.50	18.9	..	..
28.4	9.40	22.4	..	..
29.8[b]	...	21.5	5.07	7.8
31.0	9.45	23.9	5.66	8.5
33.0	9.25	22.4	5.71	8.4
37.7	9.30	23.9	..	..
40.3[b]	...	..	5.62	9.1
44.7	9.10	29.8	7.84	13.9
46.6[b]	...	25.5	6.47	10.8
48.1[b]	...	..	5.96	11.0
60.7	8.90	30.6	6.59	10.6

[a] Oxygen and CO_2 in mmoles/100 g. latex solids, NaOH and CO_2 titers in meq./100 g. [b] Samples designated thus from a different lot of latex.

A pooled sample of serum from the aliquots used for determination of volatile acid was distilled to recover sufficient material for identification. Preliminary examination of a portion of this on a silica column containing brom cresol green as indicator,[13] gave no evidence of the presence of acids of higher molecular weight than acetic. Elution with 5% *n*-butanol in chloroform yielded two approximately equal fractions, the first of which had the mobility of acetic acid. Another portion was then separated quantitatively on a silica column in which the fixed phase was 0.5 *N* sulfuric acid,[14] using 7.5% *t*-amyl alcohol in chloroform as eluent, and titrating 5-ml. fractions with 0.01 *N* NaOH. The result of this separation is compared in Fig. 2 with that of a known mixture of 0.8 meq. of acetic acid with 0.5 of formic. From the figure the fraction of formic acid in the unknown mixture is 41.5%. When a separate sample was oxidized with mercuric chloride,[12,15] the per cent. formic acid found was 42.5%.

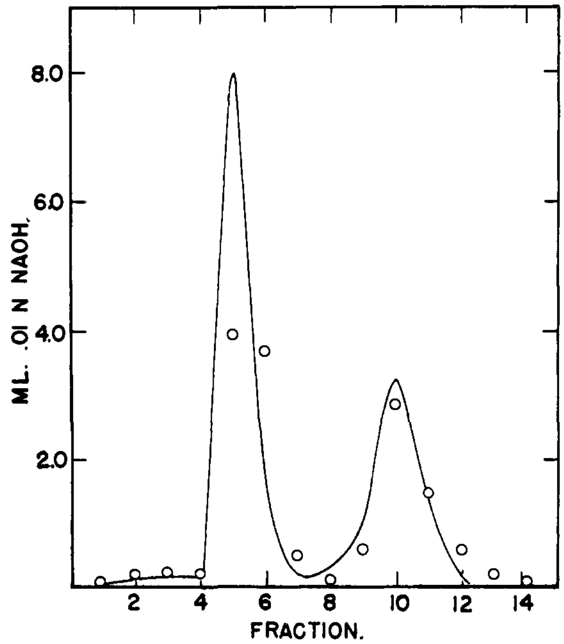

Fig. 2.—Separation of volatile acids: circles, mixture obtained from latex; solid line, known mixture of acetic (first peak) and formic acids.

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(11) W. C. Carter, R. L. Scott and M. Magat, THIS JOURNAL, **68**, 1480 (1946).

(12) M. W. Philpott and K. C. Sekar, *J. Rubber Research Inst. Malaya*, **14**, 93 (1953).

(13) S. R. Elsden, *Biochem. J.*, **40**, 252 (1946).

(14) W. A. Bulen, J. E. Varner and R. C. Burrell, *Anal. Chem.*, **24**, 187 (1952).

(15) Association of Official Agricultural Chemists, "Official Methods of Analysis," 7th ed., Washington 4, D. C., p. 460.

The pooled sera used as starting material contained an average of 12 μeq. per gram. Assuming that acetic and formic acids are produced in equivalent amounts during oxidation and correcting for acetic acid already present in the oxidized latex (1.4 μeq. per gram of serum) the calculated fraction of formic acid is 44%.

Results

The results of the determination of scission efficiency, total acid, carbon dioxide and other volatile acid as a function of oxygen consumed by the latex are given in Tables I through III[16] and plotted in part in Figs. 1 and 3, with appropriate corrections for amounts originally present. The curve for CO_2 does not pass through the origin because some carbon dioxide (about 0.5 meq./100 g. latex solids) is evolved on heating in the absence of oxygen.

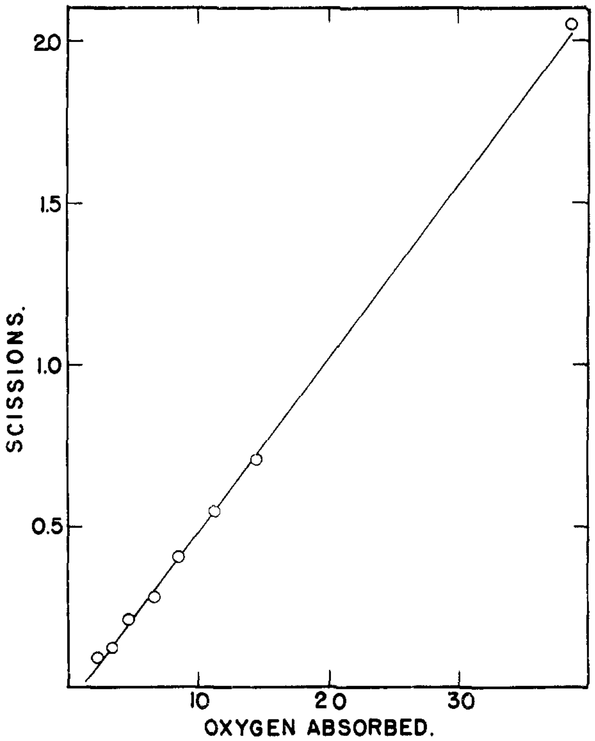


Fig. 3.—Chain scissions as a function of oxygen absorbed, both in mmoles/100 g. latex solids.

Each of these quantities is a linear function of oxygen absorbed within experimental error. The slopes of the plots of scissions, CO_2 and volatile acid as a function of oxygen are: scissions/O_2 = 0.054 mole/mole; CO_2/O_2 = 0.108 mole/mole; acid/O_2 = 0.095 eq./mole.

From these quantities the ratios of acids to scissions may be calculated: CO_2/scissions = 2.02 moles/mole; acid/scissions ≈ 1.75 eq./mole.

Discussion

Knowing that the volatile acid consists of equal amounts of acetic and formic, we have to account for the production of two molecules of carbon dioxide, one of acetic, and one of formic acid for every scission of the hydrocarbon chain. This can be accomplished in a reasonably satisfactory manner if it is assumed that the primary oxidation product of rubber is a cyclic diperoxide having the structure indicated by the results of the work of Bolland and Hughes[4] with low molecular weight polyisoprenes. (It may be noted here that squalene, oxidized under the conditions used in this work, gives yields of total acid and of carbon dioxide close to those found for rubber.)

TABLE II

VOLATILE ACID PRODUCED DURING OXIDATION

Oxygen absorbed, mmoles/100 g. TS	Volatile acid,[a] meq./100 g. TS	Oxygen absorbed, mmoles/100 g. TS	Volatile acid,[a] meq./100 g. TS
12.8	1.24	38.4	3.72
18.8	1.60	43.2	3.95
21.6	1.96	47.5	4.29
32.0	3.78		

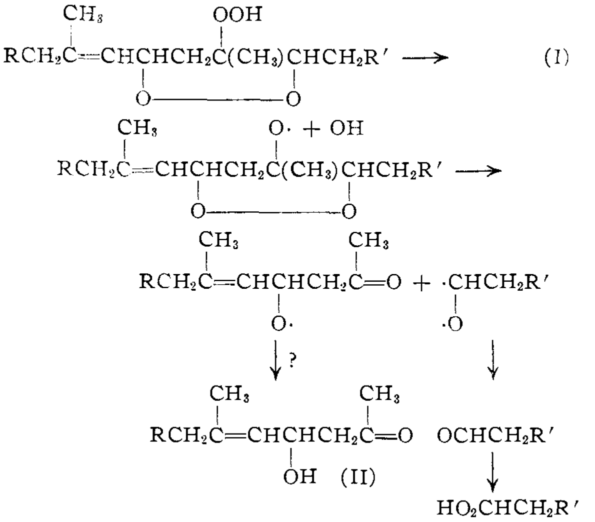
[a] Corrected for blank, 0.45 meq./100 g. TS.

TABLE III

CHAIN SCISSION BY OXYGEN

Oxygen absorbed, mmoles/100 g. T.S.	[η] (in $CHCl_3$)	Chain scissions, mmoles/100 g. T.S.	Oxygen absorbed, mmoles/100 g. T.S.	[η] (in $CHCl_3$)	Chain scissions, mmoles/100 g. T.S.
0	5.65	0	6.8	2.33	0.28
1.4	3.94	0.077	7.1	2.22	.30
2.3	3.68	.090	8.5	1.91	.40
2.9	3.35	.12	11.3	1.63	.54
3.5	3.22	.13	14.5	1.39	.70
4.8	2.65	.21	38.7	0.73	2.05
5.5	2.65	.21			

The initial product I is a tertiary hydroperoxide which is assumed to undergo total oxidative destruction following dissociation of the hydroperoxide group



$$RCH_2C(CH_3){=}CHCH(O\!-\!)CH_2C(OOH)(CH_3)CH(\!-\!O)CH_2R' \longrightarrow \quad (I)$$

$$RCH_2C(CH_3){=}CHCH(O\!-\!)CH_2C(O\cdot)(CH_3)CH(\!-\!O)CH_2R' + OH \longrightarrow$$

$$RCH_2C(CH_3){=}CHCH(O\cdot)CH_2C(CH_3){=}O + \cdot CH(\cdot O)CH_2R'$$

$$\downarrow ? \qquad\qquad \downarrow$$

$$RCH_2C(CH_3){=}CHCH(OH)CH_2C(CH_3){=}O \ (II) \qquad OCHCH_2R' \longrightarrow HO_2CHCH_2R'$$

In the absence of any information about the oxidation of compounds of the structure (II), we can only speculate on the details of its further oxidation, rapid compared with attack on the hydrocarbon itself. Assuming stepwise degradation from the terminal methyl ketone, the final products, arranged in the same order as the carbon atoms of formula II above, will be

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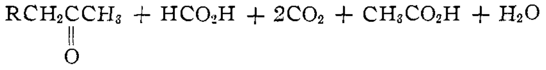
[16] Scissions, as given in Table III, are *net* scissions. The possibility of the effect of cross-linking is discussed in the first paper on scission: E. M. Bevilacqua, THIS JOURNAL, **77**, 5394 (1955).



$$RCH_2\overset{}{\underset{\overset{\|}{O}}{C}}CH_3 + HCO_2H + 2CO_2 + CH_3CO_2H + H_2O$$

The scheme outlined here is consistent with all known features of the reaction. The postulated end groups on the severed hydrocarbon chains are in reasonable agreement with published analyses[17] of highly oxidized hevea, and the known rapid oxidation of aldehydes at the temperature used here.[18] The yields of volatile materials are in the proportions found by experiment. The scheme requires six molecules of oxygen for each scission of the hydrocarbon chain, in good agreement with the limiting value found on rapid oxidation of dry rubber at high temperatures.[16]

The total amount of oxygen consumed (18.5 moles/mole of scissions) at the temperature of these experiments is much larger than that required for the scission reaction. Most of the additional oxygen appears in hydroxyl[17] and, probably, ether[18] groups. It is not clear whether the ratio of oxygen required for scission to the total is a measure of the relative amount of hydroperoxide having the structure assumed by Bolland and Hughes to predominate, or if this structure decomposes by alternate paths of which only one involves thermal scission of the tertiary alkoxy group with consequent scission of the hydrocarbon as a whole. In view of the good agreement between the postulated mechanism and the oxygen requirements at high temperature and of the decreasing yield of scission as the temperature is lowered,[8,16] the second alternative may be correct.

PASSAIC, NEW JERSEY

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[17] R. F. Naylor, *Trans. Inst. Rubber Ind.*, **19**, 45 (1944).

[18] G. R. Mitchell and J. Reid Shelton, *Ind. Eng. Chem.*, **45**, 386 (1953).

[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

The Reaction of Isopropylmagnesium Chloride with Vinylacetic and Crotonic Acids

BY F. F. BLICKE AND HAROLD ZINNES[1,2]

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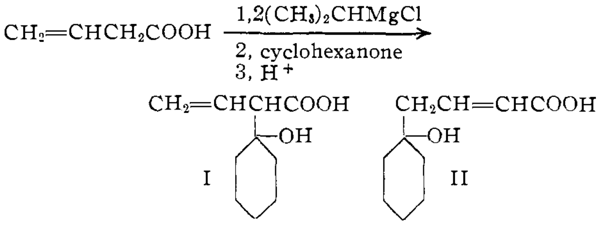
The Ivanov reagent, obtained from vinylacetic acid and isopropylmagnesium chloride, reacted with cyclohexanone to yield γ-(1-hydroxycyclohexyl)-crotonic acid. The 1,4-addition of isopropylmagnesium chloride to crotonic acid was observed.

It was found that after reaction of isopropylmagnesium chloride with vinylacetic acid, with the expectation that an Ivanov reagent, $CH_2{=}CHCH(MgCl)COOMgCl$, might be formed, and addition of cyclohexanone to the reaction mixture, an acid (m.p. 127–129°) was obtained which we thought might be the unknown α-(1-hydroxycyclohexyl)-vinylacetic acid (I). The analytical data and the neutralization equivalent found corresponded to the calculated data for this compound. If the product did not possess structure I, it seemed that the only other structure which it might possess would be that of γ-(1-hydroxycyclohexyl)-crotonic acid (II). It was reported[3] that the crotonic acid, which Dreiding and Pratt had obtained by another procedure, melted at 127–128.5°. We synthesized II by the described process[3] and found that the mixed melting point of the two acids was 127–129°.



Presumably the formation of II in the Ivanov reaction was the result of an allylic rearrangement of the Ivanov reagent. Rearrangements of this type

$$CH_2{=}CHCH(MgCl)COOMgCl \rightleftarrows CH_2(MgCl)CH{=}CHCOOMgCl$$

which involve other Grignard reagents are well known.[4] In view of the equilibrium which may exist between the two forms of the Ivanov reagent, it is not impossible that compound I may have been produced to some extent; compound II was isolated in only 22% yield.

The interaction of crotonic acid with two molecular equivalents of isopropylmagnesium chloride resulted in the formation of an intermediate IV which yielded β-isopropylbutyric acid (V), α-(1-hydroxycyclohexyl)-β-isopropylbutyric acid (VI)[5] and α-(phenylcarbamyl)-β-isopropylbutyric acid (VII) when it was treated with water, cyclohexanone and phenyl isocyanate, respectively. The formation of IV probably took place through the 1,4-addition of isopropylmagnesium chloride to the chloromagnesium salt III followed by a tautomeric rearrangement.[6]

The boiling point of the liquid acid V corre-

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[1] This paper represents part of a dissertation submitted by Harold Zinnes in partial fulfillment of the requirements for the Ph.D. degree in the University of Michigan, 1955.

[2] American Foundation for Pharmaceutical Education Fellow.

[3] A. S. Dreiding and R. J. Pratt, THIS JOURNAL, **75**, 3717 (1953).

[4] See E. R. Alexander, "Principles of Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 287–292; M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, pp. 1133–1158.

[5] Two acids were obtained. The analytical data and the neutralization equivalent obtained in the case of each acid corresponded to that calculated for VI. We believe that the acids were diastereoisomers.

[6] A similar explanation was offered by C. D. Nenitzescu (*Bull. soc. chim. Romania*, **12**, 48 (1930); *C.A.*, **25**, 1509 (1931)) to account for the formation of N-ethyl-α-acetyl-β,β-diphenylpropioanilide. In order to obtain this substance, phenylmagnesium bromide was allowed to react with N-ethylcinnamanilide, and acetyl chloride then was added to the reaction mixture.