

recovered pentenes were 70.7% pentene-1 and 29.3% pentene-2.

Hexene-1 (0.020 mole), methyldichlorosilane (0.0123 mole) and 3×10^{-8} mole of chloroplatinic acid were sealed into a glass tube. An exothermic reaction occurred at about room temperature. About 0.5 hour later the tube was chilled in Dry Ice and opened. Pentene-1 (0.043 mole) was added. The tube was resealed and heated to 140° for 2 hours. The gas chromatogram in this case showed that the pentenes were 6% pentene-2. No pentylsilanes were detected.

A similar experiment was carried out with pentene-1 instead of hexene-1 above. The tube was opened after

the reaction and evacuated to remove as much as the volatile compounds as possible at room temperature. 3-Methylbutene-1 was added to the tube. After 2 hours at 140°, the 3-methylbutene-1 (97%) was recovered along with 2.2% 2-methylbutene-2 and 0.4% 2-methylbutene-1.

Acknowledgment.—The authors wish to express their appreciation to Lee Nelson and Janet Gardner for carrying out some of the preparative work, and to Robert Winger for his assistance in analysis by gas-liquid phase chromatography.

[CONTRIBUTION OF THE CHEMISTRY DEPARTMENT, OHIO UNIVERSITY, ATHENS, OHIO]

The Kolbe Electrolysis as a Source of Free Radicals in Solution. III. Some Aspects of the Stereochemistry of the Electrode Process

BY WILLIAM B. SMITH AND HANS-GEORG GILDE

RECEIVED AUGUST 12, 1960

The electrolysis of a methanolic solution of potassium propionate in the presence of butadiene yields the *trans* isomer only of 4-octene. Replacement of the propionate by optically active 2-methylbutanoic acid gave a fraction containing a $C_{16}H_{30}$ hydrocarbon which was not optically active nor was the ozonolysis product, 3-methylpentanoic acid. The electrolysis of a methanolic solution of potassium acetate in the presence of cyclohexadiene was found to result in both *cis*- and *trans*-1,2- and 1,4-addition of methyl groups to the diene.

Previous reports from this Laboratory¹ have established that the free radicals produced during the Kolbe electrolysis of potassium acetate will readily add to dienes and will cause vinyl polymerization. Several items mentioned in these reports have led us to investigate further the stereochemistry of the electrode process.

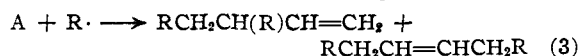
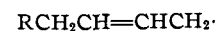
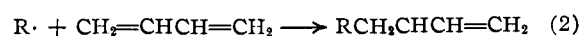
The first oddity noted was the fact that the electrolysis of a methanolic solution of potassium acetate in the presence of butadiene gave the *trans* isomer only of 3-hexene within the limits of infrared analysis and vapor phase chromatography (v.p.c.).² Replacement of the butadiene by isoprene led to the *cis* isomer only of 3-methyl-3-hexene. The polymerization of vinyl acetate during the electrolysis of potassium acetate produced a polymer which was unusually hard and brittle for its intrinsic viscosity. The polymer was shown to be neither isotactic nor highly cross linked suggesting, therefore, a high molecular weight linear structure.

In order to confirm the above data the electrolysis of potassium propionate in the presence of butadiene has now been carried out. The product work-up and examination was conducted as previously described.^{1a} The infrared spectral examination of the appropriate hydrocarbon fractions gave evidence of the formation of the *trans* isomer only of 4-octene. No bands characteristic of the *cis* isomer could be found.

The formation of the unsaturated hydrocarbons during the electrolysis of a carboxylate in the presence of a diene radical acceptor has been previously pictured as

(1) For preceding papers in this series see W. B. Smith and H.-G. Gilde, (a) *J. Am. Chem. Soc.*, **81**, 5325 (1959); (b) **82**, 659 (1960).

(2) Subsequent to the work reported in ref. 1a a more specific search for *cis*-3-hexene was carried out with the aid of an authentic sample of this material. No positive evidence for its existence in the reaction was found by either infrared spectroscopy or by v.p.c. Use of the authentic sample established the limit of detectability of *cis*-3-hexene at something less than 5% of the hydrocarbon fraction.



Surprisingly, no reports of the stereochemistry of simple 1,4-radical addition to butadiene are given in the literature. The subject has received consideration in the polymerization of butadiene, however. The data have been reviewed by Walling.³ Here it has been observed that at room temperature the *cis* structure comprises about 33% of the 1,4-addition polymer. Evidence is available to support the view that allylic radicals of the type A above maintain their steric integrity. Walling, Jacknow and Thaler⁴ have reported that the allylic chlorination of *trans*-2-butene with *t*-butyl hypochlorite yields only *trans*-1-chloro-2-butene and none of the *cis* isomer, while *cis*-2-butene gives only the *cis* isomer of 1-chloro-2-butene.

In discussing the double bond character of the 2,3-carbon bond in butadiene, Pauling has stated that the *s-trans* conformation of the molecule is more stable than the *s-cis* form.⁵ Pritchard and Sumner⁶ have given the value of 4 kcal./mole for the energy of interconversion. In contrast, Nikitin and Yakovleva⁷ have concluded on the basis of a

(3) Cheves Walling, "Free Radicals in Solution," John Wiley and Sons, Inc. New York, N. Y., 1957, pp. 228-232.

(4) C. Walling, B. B. Jacknow and W. Thaler, Abstracts, 136th National Meeting, American Chemical Society, Atlantic City, N. J.

(5) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 3rd ed., 1960, pp. 290-292.

(6) H. O. Pritchard and F. H. Sumner, *Proc. Roy. Soc. (London)*, **A235**, 136 (1956).

(7) V. N. Nikitin and T. V. Yakovleva, *Zhur. Fiz. Khim.*, **28**, 697 (1954).

study of the Raman spectrum that the *s-cis* form of isoprene comprises about 85% of the mixture. Thus, it seems reasonable to expect that the 1,4-addition of free radicals to butadiene and to isoprene should lead to a mixture of *cis* and *trans* forms.

From our data, the failure to isolate any *cis* isomer when butadiene acts as the acceptor or any *trans* isomer with isoprene suggests the operation of some external controlling factor since it seems unlikely that either butadiene or isoprene exists solely in their preferred conformations. All of the electrolyses described here and in preceding papers were conducted with smooth platinum electrodes. It is proposed that the above results are best explained by assuming that the radical acceptor is adsorbed on the surface of the electrode in its most stable conformation at the time that radical attack occurs. Thus, only *trans*-1,4-addition products have been isolated from butadiene and only *cis*-1,4-products from isoprene.

The next point of attack on the problem was designed to answer the question of how free were the radicals generated by the electrolysis before their attachment to the radical acceptor. The fact that the electrolysis of (+)- α -methylbutyric acid produces inactive 3,4-dimethylhexane^{8,9} is frequently cited as evidence that free radicals do not preserve their steric configuration.

A preliminary set of experiments was run using potassium α -methylbutyrate and a methanol solution of butadiene. Reduction with lithium aluminum hydride, chromatography over alumina, and analysis by infrared spectroscopy and v.p.c. failed to yield any fraction corresponding to the 1,4-addition of *sec*-butyl radicals to butadiene. However, examination of the higher boiling hydrocarbon material did give a fraction which had the molecular weight, hydrogenation equivalent and analysis of C₁₆H₃₀. This product arises by the attack of a *sec*-butyl radical on butadiene followed by coupling of the new radical. When subjected to ozonolysis, this hydrocarbon gave 3-methylpentanoic acid.

The above experiment was then repeated using optically active α -methylbutyric acid. The hydrocarbon portion of the reaction product was not optically active nor was the 3-methylpentanoic acid, obtained by ozonolysis.

This result can only mean that the *sec*-butyl radicals formed in the presence of butadiene are no more intimately bound in a configuration-holding interaction than those which engage in the normal Kolbe coupling reaction.

Additional evidence concerning the stereochemistry of the radical attack was sought by using a diene in which the configuration both of the starting material and the final products was known or could be ascertained. Toward this end we have electrolyzed methanolic solutions of potassium acetate in the presence of 1,3-cyclohexadiene.

(8) E. S. Wallis and F. H. Adams, *J. Am. Chem. Soc.*, **55**, 3838 (1933).

(9) H. J. Dauben, Jr., and L. Xiao-Tian, *Acta Chim. Sinica*, **25**, 129 (1959).

The hydrocarbon portion of the reaction was isolated and hydrogenated. Seven bands were obtained on v.p.c. of this material. By a combination of fractional distillation, v.p.c. and infrared spectral analysis, it was shown that cyclohexane, methylcyclohexane, *cis*- and *trans*-1,2-dimethylcyclohexane, *cis*- and *trans*-1,4-dimethylcyclohexane, and a mixture of methylcyclohexyl methyl ethers were present. The composition of the mixture is given in Table I in the Experimental section.

The experiments with cyclohexadiene were carried out to test the postulation that the diene might be adsorbed in a flat position on the surface of the electrode at the time of attack by the electrolytically generated free radicals. The addition of a methyl free radical to cyclohexadiene leads to the formation of an allylic free radical which is perforce *cis* in structure. The subsequent addition of the second methyl radical leads to no preferential arrangement of the methyl groups in an all-*cis* or all-*trans* fashion in either the 1,2- or the 1,4-addition products. These results do not negate the possibility of adsorption of the diene on the electrode, for if the allylic radical A is desorbed before its further reaction or if the diene is adsorbed in a position perpendicular to the electrode the same results would be obtained. The possibility that reaction with cyclohexadiene occurs entirely in the solution cannot be ruled out, though it seems unlikely from our results with the open-chain dienes.

The higher boiling material in the hydrocarbon fraction of the cyclohexadiene reaction produced two bands on v.p.c. which careful fractional distillation failed to separate. This material gave a broad band in the infrared between 1060 and 1150 cm.⁻¹ and produced a positive Zeisel test for an alkoxy group. The carbon-hydrogen analysis was that of a mixture of methyl substituted methoxycyclohexanes. While the exact nature of the components was not further elucidated, it is evident from the above that some methyl ethers were being produced in the reaction.

This observation is of some interest since it represents the first occasion in which the formation of ethers has been encountered in our work. Ethers have been reported frequently as by-products of the Kolbe electrolysis though they are not the expected product from the attack of free radicals on the alcohol solvent. Bauld¹⁰ has recently shown that these by-products arise from the further oxidation of the electrolytically produced radicals to carbonium ions which then attack the solvent. It seems reasonable that the ethers here arise in the same fashion.

Acknowledgment.—This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

Experimental

The apparatus and techniques used in this research have been described previously.^{1a} Three columns used for vapor

(10) N. L. Bauld, Thesis, University of Illinois, 1959; see also ref. 3, p. 581.

phase chromatography were: I, tricresyl phosphate on firebrick; II, 40% β,β' -oxydipropionitrile on Chromosorb; and III, 30% Apiezon L on Chromosorb. Whenever possible the infrared spectra were compared with those contained in the A.P.I. tables.¹¹ The appropriate serial numbers are given in parentheses.

The Electrolysis of Potassium Propionate in the Presence of Butadiene.—Solutions of potassium propionate (110 g.) in 550 ml. of methanol and 140 ml. of butadiene were electrolyzed at a current of 1.1–1.5 amperes for 11–16.5 hr. During the reaction the pH was maintained at approximately 7 by the addition of propionic acid.

The product was worked up as previously described.^{1a} The yield of crude product was 9.5–13 g. The material (24.9 g.) from two runs was combined and treated with 5 g. of lithium aluminum hydride in 300 ml. of ether. The reduction product was chromatographed over 500 g. of chromatographic grade alumina made up in petroleum ether (20–40°). The column was washed with 1 l. of petroleum ether which, upon distillation, gave 5 g. of crude hydrocarbon material, fraction I. Elution of the column with 1 l. of methanol gave, after distillation, 3.7 g. of a crude mixture of alcohols, fraction, II.

Slow distillation of fraction I through a semi-micro column produced nine cuts boiling over the range 34 to 194°. Cut 5 (0.3 ml.) had b.p. 114–121°, n_D^{25} 1.4104; reported¹² for *trans*-4-octene, b.p. 120.7°, n_D^{25} 1.4110.

The v.p.c. analysis of cut 5 was carried out on column III at 160°. Three bands were produced of which the second comprised 94% of the total. The infrared spectrum of this cut agreed well with that of *trans*-4-octene¹¹ (822) with characteristic bands at 9.11, 9.42 and 11.16 μ . While no bands attributable to *cis*-4-octene¹¹ (938) were found, some weak bands, characteristic of vinyl absorption bands, were present.

The materials in fraction II were hydrogenated in ethanol using Adams platinum until no test with permanganate was given. Careful distillation of this material, as before, gave no pure fractions. A cut, b.p. 165–185°, was subjected to v.p.c. at 160° through column III. Seven bands were obtained. Of these, band 4 (29.1%) and band 5 (41.5%) were clearly the major components of the mixture. These were tentatively identified as 2-ethyl-1-butanol and 1-hexanol by comparison of retention times with authentic sample. The infrared spectrum of a 40–60 mixture of these two alcohols agreed very closely with that of the material in this cut.

The Electrolysis of Potassium α -Methylbutyrate in the Presence of Butadiene.—A solution of the potassium salt (50 g.) of α -methylbutyric acid in 250 ml. of methanol and 100 g. of butadiene was electrolyzed at 1.5 amperes for 7 hr. The reaction was worked up as before yielding 7.5 g. of crude product.

The gas produced during the electrolysis was collected over water. This material was subjected to v.p.c. at 24° over column II. By a comparison of retention times with authentic samples it was shown that this material consisted of butane (24%), 1-butene (5%), *trans*-2-butene (6%), *cis*-2-butene (3%) and butadiene (62%). Presumably, carbon dioxide came off with the air peak.

The products of four runs (34 g.) were combined and reduced as before with lithium aluminum hydride. Chromatography over alumina produced 7 g. of hydrocarbon fraction and 4.5 g. of alcohol fraction.

A portion (1.5 g.) of the hydrocarbon fraction was hydrogenated with Adams catalyst. This material on v.p.c. at 127.5° through column I produced two bands. The first band corresponded in retention time to authentic 3,4-dimethylhexane. Furthermore, the infrared spectrum of this material showed all of the bands of authentic 3,4-dimethylhexane. The second component in the mixture was not specifically identified. However, a search for 3-methylheptane, with the aid of an authentic sample, failed to reveal the presence of this substance.

The remaining unsaturated hydrocarbon was distilled through a semi-micro column. A cut, b.p. 205–226°, was isolated (2.3 ml.), which gave a hydrogenation equivalent

of 109 (calcd. for $C_{16}H_{30}$, 111), molecular weight 200 (calcd. for $C_{16}H_{30}$, 222), and only one band on v.p.c. at 127.5° through column I.

Anal. Calcd. for $C_{16}H_{30}$: C, 86.40; H, 13.60. Found: C, 86.35; H, 13.88.

Ozonolysis of this cut by the method of Henne¹³ gave an acid fraction, b.p. 200° (0.1 ml.), n_D^{25} 1.4217; reported¹⁴ for 3-methylpentanoic acid, b.p. 197.2–197.4°, n_D^{25} 1.4159. The neutralization equivalent was 127 on a very small sample (calcd. for 3-methylpentanoic acid, 116).

Since the $C_{16}H_{30}$ cut represented the major component of the high boiling hydrocarbon, in subsequent experiments the entire hydrocarbon fraction was ozonized. In this fashion, one could isolate up to 1 g. of 3-methylpentanoic acid, b.p. 196–208°, which gave an infrared spectrum identical to that of a known sample.

The alcohol fraction was given only a cursory examination. Infrared and v.p.c. analysis established the presence of active amyl alcohol. However, the several other components were not identified.

The Electrolysis of Sodium (+)- α -Methylbutyrate.—The above electrolysis was repeated using sodium (+)- α -methylbutyrate, prepared by oxidizing active amyl alcohol obtained from fusel oil. The acid had the following properties: b.p. 58–59° (2–3 mm.), n_D 1.4030, and α_D^{25} + 12.98° (*l* 1, neat); reported^{15,16} for (+)- α -methylbutyric acid, n_D^{25} 1.4030, α_D^{25} + 17.85° (*l* 1, neat). Thus, the acid prepared in this fashion was 79% optically pure. Its infrared spectrum was identical with that of a sample of the (\pm)- α -methylbutyric acid.

The optically active acid was diluted with (\pm)-acid to a final value of α_D^{25} + 5.95° (*l* 1, neat), and this was converted to the sodium salt with bicarbonate. The anhydrous salt was obtained by evaporating the water under vacuum.

Three electrolyses were conducted as described above using the optically active salt. The combined yield of crude product was 15 g., α_D^{25} + 0.07° (*l* 1, neat). This material was treated with lithium aluminum hydride and chromatographed as before; yield of hydrocarbon fraction, 3.8 g., α_D^{25} 0.0° (*l* 1, neat). Ozonolysis gave a small amount of slightly impure 3-methylpentanoic acid, n_D^{25} 1.4168, $[\alpha]_D^{25}$ 0.0° (acetic acid).

The crude alcohol fraction from the above chromatograph gave α_D^{25} – 0.03° (*l* 1, neat).

The Electrolysis of Potassium Acetate in the Presence of Cyclohexadiene.—A mixture of 50 g. of potassium acetate, 27 g. of cyclohexadiene¹⁷ and 250 ml. of methanol was electrolyzed under a nitrogen atmosphere for 12–15 hours at 1.5 amperes. The pH was maintained at 7 by the occasional addition of acetic acid. The yield of crude product, after the usual work-up, was 9.5–12 g.

The combined yield of four runs was reduced with lithium aluminum hydride and chromatographed over alumina to produce 14.5 g. of hydrocarbon material and 19.2 g. of an alcohol mixture.

Attempts at fractioning the hydrocarbon mixture produced no pure fractions. The entire fraction was then hydrogenated using Adams catalyst in acetic acid. The saturated product produced seven bands on v.p.c. at 106° through column I. The retention times and percentage compositions are reported in Table I. By extremely slow distillation through a spinning band column, it was possible to concentrate the individual components into fractions containing 60–80% of material corresponding to one of the v.p.c. bands. The following fractions were isolated: (a) b.p. 81–90°, (b) 97.5–119.5°, (c) 119.5–121.5°, (d) 123.5–124.5°, (e) 128.5–132.5°, and a higher boiling residue.

By means of infrared analysis, the principal constituent of each cut was identified. Each was identified by at least four characteristic bands. The appropriate A.P.I. references are also given in Table I. In this fashion it was found that cut (a) was predominantly cyclohexane, (b) methylcyclohexane contaminated with *trans*-1,4-dimethylcyclo-

(13) A. L. Henne and P. Hill, *J. Am. Chem. Soc.*, **65**, 762 (1943).

(14) M. Hommelen, *Bull. soc. chim. Belge*, **42**, 243 (1933).

(15) J. Kenyon, H. Phillips and V. P. Pittman, *J. Chem. Soc.*, 1072 (1935).

(16) J. Brenner and K. Mislow, *J. Org. Chem.*, **21**, 1312 (1956).

(17) K. Ziegler, A. Spaeth, E. Schaaf, W. Schumann and E. Winkelmann, *Ann.*, **561**, 110 (1942).

(11) "Catalog of Infrared Spectral Data," Am. Petroleum Inst. Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pa., 1947.

(12) G. Egloff, "Physical Constants of Hydrocarbons," Reinhold Publishing Corp., New York, N. Y., 1939, p. 216.

TABLE I
ANALYSIS OF THE HYDROCARBON FRACTION FROM CYCLO-
HEXADIENE

V.p.c. band	Reten- tion time, min.	%	Compound	A.P.I. ¹¹ ref.
1	5.4	2	Cyclohexane	368
2	8.0	2	Methylcyclohexane	369
3	10.4	14	<i>trans</i> -1,4-Dimethylcyclohexane	304
4	12.4	27	<i>trans</i> -1,2-Dimethylcyclohexane	300
			<i>cis</i> -1,4-Dimethylcyclohexane	303
5	15.5	15	<i>cis</i> -1,2-Dimethylcyclohexane	371
6	33.8	19
7	39.8	20

hexane, (c) essentially pure *trans*-1,4-dimethylcyclohexane, (d) *trans*-1,2- and *cis*-1,4-dimethylcyclohexane, and (e) *cis*-1,2-dimethylcyclohexane.

Distillation of the high boiling residue gave two additional fractions: (1) b.p. 148.5–149.5°, and (2) b.p. 160–175°. The v.p.c. of these at 154° through column I showed that each contained the same two components in the ratio 84%–16% for (1) and 25%–75% for (2). Both fractions gave a positive Zeisel test readily, and each had a broad ether band in the infrared at 1060–1150 cm.⁻¹. The carbon–hydrogen analysis for each fraction was determined. *Anal.* Found: (1) C, 75.43; H, 13.52. Found: (2) C, 76.36; H, 12.94.

The alcohol portion of the reaction product was hydrogenated with Adams catalyst and then distilled: (1) b.p. 161–162°, (2) b.p. 162–168°, and a higher boiling residue. The v.p.c. of each cut showed the same four bands with one component making the principal contribution (44%). This was identified as 4-methylcyclohexanol by a comparison with the retention time and infrared spectrum of an authentic sample (characteristic bands at 7.48, 9.90, 10.52 and 12.70 μ). A search by v.p.c. and infrared, with the aid of authentic samples, failed to reveal any evidence for the presence of cyclohexanol or 2-methylcyclohexanol.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY, PITTSBURGH 13, PENNA.]

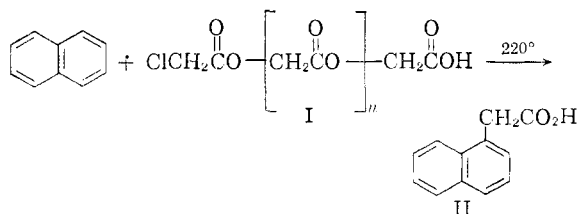
Direct Aromatic Carboxymethylation with Chloroacetylpolyglycolic Acids. Orientation in Dibenzofuran as Evidence of a Free Radical Mechanism¹

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RECEIVED SEPTEMBER 9, 1960

Direct carboxymethylation of dibenzofuran by heating with chloroacetylpolyglycolic acids gave a mixture of dibenzofuranacetic acids consisting of the 1-acetic acid (*ca.* 55%), the 4-acetic acid (*ca.* 30%) and the 3-acetic acid (*ca.* 15%). This isomer distribution is entirely unlike the large preponderance of the 2-substitution product typical of electrophilic substitutions of dibenzofuran, but nearly identical to that observed in a less efficient free-radical carboxymethylation of dibenzofuran by acetic acid and di-*t*-butyl peroxide. It agrees qualitatively with predictions based upon molecular orbital calculation of free-radical localization energies. Apparently aromatic carboxymethylations with chloroacetylpolyglycolic acids proceed either by a free-radical mechanism or, less probably, by reactions between undissociated molecules which duplicate the characteristic orientation of the equivalent free-radical substitution. Carboxymethylation of phenanthrene with chloroacetylpolyglycolic acids yielded chiefly 9-phenanthreneacetic acid. With anthracene attack was evidently at the 9 and 10-positions, producing mixed acids and some 9,10-dimethylanthracene. A very small yield of the expected arylacetic acid mixture was produced from dibenzothiophene, essentially none from carbazole, quinoline or acridine. Much of the quinoline was converted into an acid-soluble amorphous solid. Photochemical carboxymethylation by thioglycolic acid failed with dibenzofuran, but succeeded with pyrene. Catalysis of the conversion of chloroacetic acid into polymers of the chloroacetyl-polyglycolic acid type was observed with lithium chloride, lithium bromide, potassium chloride, potassium carbonate and potassium bromide, but not with sodium chloride.

In an earlier report from this Laboratory⁴ there was described a reaction between naphthalene and certain glycolic acid polymers which produced α -naphthylacetic acid (II) as the chief isolated product. The glycolic acid polymers, which contained some chlorine and could be described as



chloroacetylpolyglycolic acids (I), were produced by refluxing chloroacetic acid in the presence of catalytic amounts of potassium bromide. The formation of α -naphthylacetic acid by heating

chloroacetic acid with naphthalene in the presence of potassium bromide^{4–6} (and perhaps in its absence)⁷ can be attributed largely, if not entirely, to the reaction of the polymers (I) with naphthalene. The remarkable capacity of the polyesters (I) to carboxymethylate naphthalene at temperatures near 220° appeared to be a phenomenon worthy of further investigation, and the present paper is concerned with the scope and mechanism of this type of apparently uncatalyzed aromatic substitution.

In the previous paper⁴ the possibility was mentioned that an acid-catalyzed heterolytic cleavage of the polymer chain at an oxygen–methylene bond

(1) This paper is based on theses submitted by Monroe W. Munsell (1955) and Edward A. Bartkus (1959) in partial fulfillment of the requirements of the degree of Doctor of Philosophy, Carnegie Institute of Technology.

(2) Institute Fellow in Organic Chemistry, 1954–1955.

(3) Du Pont Fellow in Chemistry, 1958–1959.

(4) P. L. Southwick, L. A. Pursglove, B. M. Pursglove and W. L. Walsh, *J. Am. Chem. Soc.*, **76**, 754 (1954).

(5) P. L. Southwick (to Food Machinery and Chemical Corporation), U. S. Patent 2,655,531 (October 13, 1953).

(6) (a) Y. Ogata and I. Ishiguro, *J. Am. Chem. Soc.*, **72**, 4302 (1950); (b) Y. Ogata, I. Ishiguro and Y. Kitamura, *J. Org. Chem.*, **16**, 239 (1951); (c) Y. Ogata, M. Okano and Y. Kitamura, *ibid.*, **16**, 1588 (1951); (d) Y. Ogata, M. Inoue and Y. Kitamura, *ibid.*, **18**, 1329 (1953); (e) Y. Ogata, M. Okano, K. Matsuda and T. Shono, *ibid.*, **19**, 1529 (1954).

(7) A. Wolfram, L. Schörnig and E. Hausdorfer (to I. G. Farbenind. A.-G.) German Patent 562,391 (Feb. 1, 1929); U. S. Patent 1,951,686 (March 20, 1934).