one to determine the average number of oxygen bridges per chromic ion present in aged or heated solutions of chromic nitrate or chloride.

2. The postulated composition of a sixty-hour refluxed solution of chromic chloride and of a 1/3 basic, sixty-hour refluxed solution given by E. Stiasny[11] and co-workers has been shown to require revision.

3. Data are given for the number of MoO_4H^- groups that will coördinate to chromium in variously treated chromic salt solutions. These data show that the average number of oxygen bridges joining chromic ions increases with time on refluxing solutions of chromic nitrate and chromic chloride until a maximum is reached at sixty hours. Further refluxing does not cause any increase in the number of bridges. The addition of sodium hydroxide before refluxing causes a large increase in the number of oxygen bridges formed as does also the addition of ethyl alcohol.

SALT LAKE CITY, UTAH RECEIVED[18] AUGUST 18, 1949

(18) Original manuscript received August 20, 1947.

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

The Thermal Polymerization of Monoölefinic Compounds[1]

BY WILLET F. WHITMORE AND J. FRED GERECHT

Numerous studies of the heat bodying of drying oils have failed to yield conclusive evidence for any of the reaction mechanisms suggested for this process.[2] The thermal polymerization of methyl undecylenate had been studied by one of us[3] in the hope that a more complete understanding of the thermal reactions of this simple compound might yield information concerning the bodying of the more complex oils. In the present work an allylic free radical theory to explain the thermal transformations of simple unsaturated compounds is proposed, and some experimental support for this mechanism has been obtained from a study of two terminally unsaturated compounds, methyl undecylenate and 1-octene.

Free radicals, which might arise through chain scission or peroxidation, are capable of initiating a chain reaction by attacking a monoalkyl substituted ethylene to form a resonating allylic radical (I),[4] which in either resonance form may add to the terminal position[5] of another olefin molecule (II). Either of the resulting unsaturated dimeric radicals may then add intramolecularly to its own double bond to yield saturated cyclic radicals (III). In an analogous manner the saturated or the unsaturated dimeric radicals may continue this process of radical addition to give a variety of polymeric radicals (IV). It is also quite possible for the unsaturated trimeric radicals formed in step IV to cyclize by an addition similar to step III to form polymeric alicyclic radicals.[5a]

Any of these radicals (monomeric, dimeric or polymeric) instead of adding to another olefin molecule can terminate through chain transfer by withdrawing an α-methylenic hydrogen to yield a stable compound and a new resonating allylic radical as in I.

In an attempt to verify such a mechanism, methyl undecylenate was polymerized at 325°, and separated by distillation into monomeric, dimeric and higher polymeric fractions.[3] Each fraction was then subjected to performic acid hydroxylation[6] followed by periodate oxidation.[7] The oxidation mixtures were examined for the specific degradation products which should result if the unsaturated compounds predicted were present.

According to the mechanism indicated, the monomeric fraction should contain a certain amount of methyl 9-undecenoate, A, resulting from the reaction of one of the resonance forms of the allylic radical with an α-methylenic hydrogen, and hence, both acetaldehyde and formaldehyde should be present in the oxidation mixture. Such was found to be the case, and from the amount of acetaldehyde found[8] it was estimated that 12% of the recovered monomer had undergone a double bond shift.

Furthermore, the dimeric fraction should contain dimethyl 8-eicosene-1,20-dicarboxylate, dimer B (R = H); dimethyl 8-ethylene-octadecane-1,18-dicarboxylate, dimer C (R = H) and methyl esters of saturated acids of 22 carbon atoms containing the cyclopentane ring, D, resulting from the termination reaction of the dimeric radicals with an α-methylenic hydrogen. Previously the presence of dimer B (R = H) in this fraction has been established, and a saturated dimer believed to be cyclic also has been isolated.[3] Although methods for the recognition of either of the

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(1) From a thesis presented by J. Fred Gerecht to the Graduate School of the Polytechnic Institute of Brooklyn, June, 1948, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Sunderland, *J. Oil and Colour Chemists' Assoc.*, **28**, 137 (1945).

(3) Ross, Gebhart and Gerecht, This Journal, **67**, 1276 (1945).

(4) Smith and Taylor, *J. Chem. Phys.*, **8**, 543 (1940).

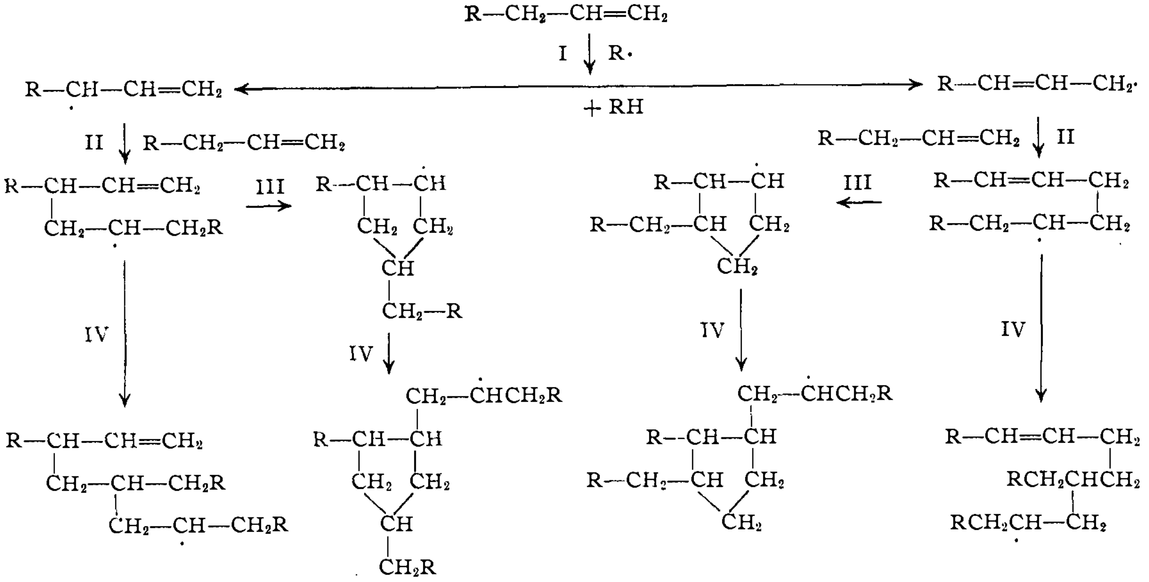
(5) Farmer, *J. Soc. Chem. Ind.*, **66**, 86 (1947).

(5a) We are indebted to one of the referees for his suggestion of this reaction of the trimeric radicals.

(6) (a) Greenspan, *Ind. Eng. Chem.*, **39**, 847 (1947); (b) Swern, Billen, Findley and Scanlan, This Journal, **67**, 1786 (1945).

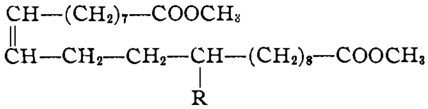
(7) Jackson, "Organic Reactions," Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 341.

(8) Shupe, *J. Assoc. Offic. Agr. Chemists*, **26**, 249 (1943).

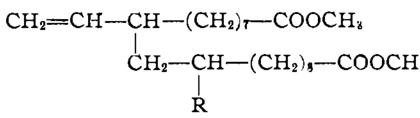


expected cyclopentane dimers, D, are lacking, McKinley, Stevens and Baldwin[9] have shown that one of the dimers resulting from the thermal polymerization of isobutylene is 1,1,3-trimethylcyclopentane. The formation of this compound may be explained more satisfactorily by an allylic radical mechanism than by any of the several sequences proposed by these authors. The presence of dimer C (R = H) would be indicated by the formation of formaldehyde in the oxidative cleavage. This aldehyde was demonstrated to be present, and from the quantity found[10] it was inferred that C comprised 12% of the dimer.

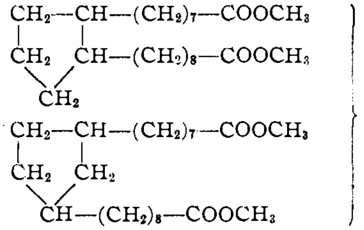
$CH_3—CH=CH—(CH_2)_7—COOCH_3$ (A)



$$\begin{array}{l} CH—(CH_2)_7—COOCH_3 \\ \| \\ CH—CH_2—CH_2—\underset{\displaystyle R}{\underset{|}{C}}H—(CH_2)_8—COOCH_3 \end{array}$$ (B)



$$\begin{array}{l} CH_2=CH—CH—(CH_2)_7—COOCH_3 \\ \qquad\quad | \\ \qquad\quad CH_2—\underset{\displaystyle R}{\underset{|}{C}}H—(CH_2)_8—COOCH_3 \end{array}$$ (C)



(D)

Although the polymer fraction, resulting from the thermal treatment of methyl undecylenate, was a complex mixture, one would also expect it to contain some of the unsaturated polymers B and C (R = one or more undecylenic units). Since polymer B has a double bond at the C_9-position and polymer C has an ethylenic side chain, hydroxylation followed by periodate cleavage of these compounds should yield both azelaic acid and formaldehyde, respectively. These degradation products were obtained and identified, although the yields were poor probably because of isolation difficulties.

Since thermal polymerization, according to this mechanism, is postulated as a free radical process, it should be possible to initiate the reaction with organic peroxides, and it was ascertained that by the addition of di-*t*-butyl peroxide the polymerization occurred at 200° instead of 325°.

In addition to the ester methyl undecylenate, the olefin, 1-octene, was also polymerized at 325° and the resulting products separated by distillation as previously indicated. Although the same amount of detailed information was not sought with this olefin, sufficient analytical data were obtained on the dimer fraction to indicate that the chemical changes are essentially the same with this hydrocarbon as with methyl undecylenate.

Although the fatty acids of the drying oils differ from the simpler compounds studied in this work by the fact that they do not possess terminal unsaturation and usually have multiple double bond structures, the authors are of the opinion that the thermal polymerization of these more complex compounds also proceeds by an allylic radical mechanism similar to the one outlined, differing only in the rate of polymerization and the variety of polymeric products. Many of the reactions of the fatty acids, such as the thermal polymerization[11] or peroxidation[12] of methyl oleate and the ability of linoleic acid to act as an inhibitor in certain free radical polymerization reactions,[13a]

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[9] McKinley, Stevens and Baldwin, THIS JOURNAL, **67**, 1455 (1945).

[10] Jonescu, *Bull. soc. chim.*, [4] **47**, 51, 1408 (1930).

[11] Bradley and Johnston, *Ind. Eng. Chem.*, **32**, 802 (1940).

[12] Ross, Gebhart and Gerecht, THIS JOURNAL, **71**, 282 (1949).

[13] (a) Wilson and Pfau, *Ind. Eng. Chem.*, **40**, 530 (1948); (b) Farmer, *J. Oil and Colour Chemists' Assoc.*, **31**, 393 (1948).

support this point of view. In addition Farmer[13b] has very recently suggested an allylic radical mechanism similar to our own to account for the thermal polymerization of the drying oils.

Experimental

Polymerization of Methyl Undecylenate and 1-Octene.—Both methyl undecylenate, b. p. 105.4° at 3.3 mm., and 1-octene (Humphrey and Wilkinson, Inc.) were polymerized at 325° and separated by distillation into monomer, dimer and higher polymer fractions according to the procedure of Ross, Gebhart and Gerecht.[3] The results with the ester were identical with those previously reported,[3] and the details of the separation of the polymerized hydrocarbon mixture are given in tabular form.

DISTILLATION OF POLYMERIZED 1-OCTENE (220 G.)

Fraction	B. p., °C.	Pressure, mm.	Wt., g.
1	115–125	760	132.0
2	to 75	2	7.8
3	75– 95	2	1.6
4	95–135	2	19.5
Residue	Above 135	2	55.0

Fractions 3 and 4 were combined and redistilled. The portion (16.6 g.) b. p. 80–90° at 0.5 mm. was collected as dimer.

Hydroxylation Procedure.—The performic acid methods of Greenspan[6a] or Swern, Billen, Findley and Scanlan[6b] were used for all hydroxylations, and the monohydroxy, monoformoxy compounds obtained were either saponified or deformylated by boiling with methanol containing 1% of sulfuric acid.

The Periodate Cleavage and Examination of Degradation Products. Methyl Undecylenate Monomer.—Iodine value 119.5, sapn. equiv. 198.5. The neutral salts obtained by the saponification of 1 g. of hydroxylated methyl undecylenate monomer were subjected to the periodate oxidation method of Shupe[8] and from the amount of acetaldehyde found by titration, it was estimated that 12% of the recovered monomer was methyl 9-undecenoate. Before heat polymerization the same procedure indicated only 0.6% of methyl 9-undecenoate.

To confirm the acetaldehyde, 5 g. of the hydroxylated monomer was treated according to Shupe's procedure, except the bisulfite absorption tubes were replaced by a 250-ml. flask containing 150 ml. of a solution of 2,4-dinitrophenylhydrazine in 2 *N* hydrochloric acid.[14] The 2,4-dinitrophenylhydrazone which formed, melted at 165° after several recrystallizations, and showed no depression when mixed with an authentic specimen of acetaldehyde 2,4-dinitrophenylhydrazone.

Methyl Undecylenate Dimer.—Iodine value 47.2, sapn. equiv. 197.5. In order to estimate the amount of C in the dimer fraction, the following modification of the method of Jonescu[10] was used. A sample (1.04 g.) of hydroxylated methyl undecylenate dimer (vicinal glycol content[8] 54%) was saponified. The salts were dissolved in water and the solution neutralized with 0.5 *N* hydrochloric acid. A solution of sodium periodate (0.5 g. H_5IO_6 in 50 ml. of water plus excess sodium bicarbonate) was added. When the oxidation was complete (three-quarters hour), the mixture was acidified with 10 ml. of glacial acetic acid, and extracted with ether to remove water-insoluble aldehydes. To the aqueous phase 2 g. of potassium iodide was added and the liberated iodine was destroyed with the required volume of sodium thiosulfate solution. Then 100 ml. of saturated "methone" solution was added, and after this mixture had stood for three-quarters hour the solid was collected on a tared crucible. It proved to be almost pure formaldehyde dimethone compound (m. p. 187–188°) and from the weight (84.8 mg.) it was estimated that the dimer contained 12% of C. Recrystallization of this crude derivative yielded pure formaldehyde dimethone compound (m. p. 190°) which did not depress the m. p. of an authentic sample.

Glycerol was treated in exactly the same way to test the accuracy of the method, and the theoretical amount of formaldehyde dimethone compound was recovered.

Methyl Undecylenate Polymer.—Iodine value 18.4, sapn. equiv. 199.0. The hydroxylated polymer acids (90 g.), obtained by saponification of the performic acid treated polymer, were dissolved in 100 ml. of ethanol, and a solution of 10 g. of periodic acid in 25 ml. of ethanol was added. The oxidation was allowed to proceed for one-half hour, and then the alcohol was distilled off under vacuum using a Dry Ice condenser. The alcohol distillate when treated with an equal volume of saturated "methone" solution gave the formaldehyde dimethone derivative m. p. 190°, mixed m. p. 190°. After removal of alcohol, the residue was taken up in ether and water and the layers separated. The ether solution was washed with water, dried over sodium sulfate, and the solvent removed on the steam-bath. The residue, a mixture of acids and aldehydes, was oxidized with peracetic acid, prepared by heating 15 ml. of 30% hydrogen peroxide with 75 ml. of glacial acetic acid for one hour at 85°.[15] The acetic acid was then distilled off in vacuum and the residue extracted with three 250-ml. portions of hot water. The combined water extracts were evaporated to dryness and yielded 0.6 g. of crude azelaic acid. The crude acid was purified by extraction with five 2-ml. portions of dry ether followed by recrystallization of the insoluble portion from ethyl acetate. The azelaic acid obtained melted 105–107°, mixed m. p. 106–107°; neutral equivalent 95.5 calcd. 94.0; *p*-bromophenacyl ester m. p. 130°, mixed m. p. 130°.

1-Octene Dimer (Iodine Value 85.3).—The dihydroxy 1-octene dimer (18.5 g.—vicinal glycol content 55%) was stirred with 55 ml. of aqueous periodic acid solution (0.180 g. H_5IO_6 per ml.) for five hours. The water-insoluble oil was then taken up in ether, and the excess oxidant destroyed with potassium iodide followed by the required amount of sodium thiosulfate solution. When a solution of "methone" was added to this solution, the formaldehyde dimethone derivative was isolated, m. p. 190°, mixed m. p. 190°. The solvent was removed from the extract on the steam-bath, and the residual aldehydes oxidized with peracetic acid[15] (10 ml. 30% H_2O_2 + 47 ml. of glacial acetic acid). The acids (8.0 g.) recovered from the oxidation by ether extraction were distilled.

Fraction	B. p., °C.	Press., mm.	Grams	Neut. equiv.	M. p.,[a] °C.
1	85– 92	6	0.43	121	....
2	92– 93	6	1.01	120	....
3	93– 94	6	0.35	119.2	70–71[b]
4	to 106	1	1.04	156.0	....
5	106–107	1	1.14	176.5	....
6	107–108	1	0.53	177.0	....
7	108–109	1	0.71	178.5	65–66[b]
Residue	Above 109	1	3.00	340	....

[a] M. p. of *p*-bromophenacyl esters. [b] Mixed m. p. no depression.

The neutral equivalents of the fractions indicated the original acids to be largely a mixture of hexanoic and decanoic acids, and the *p*-bromophenacyl esters prepared from fractions 3 and 7 confirmed the identity of the two acids.

Polymerization of Methyl Undecylenate with Di-*t*-butyl Peroxide.—One gram of di-*t*-butyl peroxide was dissolved in 95 g. of methyl undecylenate and the mixture heated under reflux at 200° for three hours. The monomer was then distilled off in vacuum and 30% of polymeric material (dimer and polymer) was obtained as a residue.

Acknowledgment.—The authors thank Drs. John Ross and Arthur I. Gebhart of the Colgate–

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(14) Brady and Elsmie, *Analyst*, **51**, 77 (1926).

(15) D'ans and Kneip, *Ber.*, **48**, 1143 (1915).

Palmolive-Peet Co. for their interest throughout the work and Dr. Turner Alfrey of this Institute for his helpful suggestions regarding the reaction mechanism.

Summary

A mechanism based on the formation and reactions of allylic free radicals has been proposed to explain the thermal transformations of simple unsaturated compounds.

Evidence which supports this allylic radical mechanism was obtained from a study of two terminally unsaturated compounds, methyl undecylenate and 1-octene.

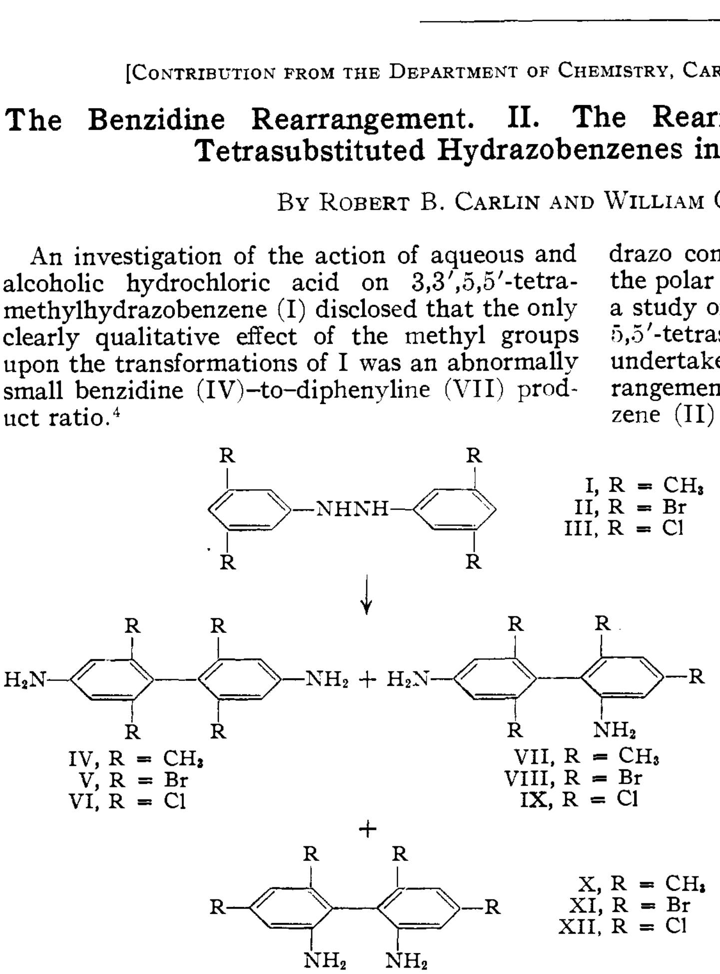
BROOKLYN 2, NEW YORK RECEIVED MARCH 18, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Benzidine Rearrangement. II. The Rearrangements of Three 3,3',5,5'-Tetrasubstituted Hydrazobenzenes in 2:1 Sulfuric Acid[1,2]

BY ROBERT B. CARLIN AND WILLIAM O. FORSHEY, JR.[3]

An investigation of the action of aqueous and alcoholic hydrochloric acid on 3,3',5,5'-tetramethylhydrazobenzene (I) disclosed that the only clearly qualitative effect of the methyl groups upon the transformations of I was an abnormally small benzidine (IV)-to-diphenyline (VII) product ratio.[4]



I, R = CH_3
II, R = Br
III, R = Cl

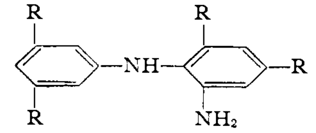
IV, R = CH_3
V, R = Br
VI, R = Cl

VII, R = CH_3
VIII, R = Br
IX, R = Cl

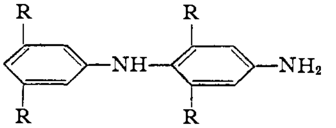
X, R = CH_3
XI, R = Br
XII, R = Cl

Other possible effects of the methyl groups, such as (1), increased disproportionation ($2ArNHNHAr \rightarrow ArN{=}NAr + 2ArNH_2$); (2), unusually severe conditions required to bring about reaction; and (3), the formation of one or both semidines (XIII and XIV, R = CH_3), were not observed. In an effort to discover the effects of other substituents upon the rearrangements of aromatic hydrazo compounds and, if possible, to distinguish the polar and steric contributions to these effects, a study of the rearrangements of a series of 3,3',5,5'-tetrasubstituted hydrazobenzenes has been undertaken; and an investigation of the rearrangements of 3,3',5,5'-tetrabromohydrazobenzene (II) and of its tetrachloro analog (III) has now been completed. Because 2:1 sulfuric acid is the best medium yet found for the rearrangement of II, and because it was desirable to be able to compare the rearrangements of I, II and III under identical reaction conditions, the rearrangements of I and III were also carried out in 2:1 sulfuric acid. In this paper, the rearrangements and related reactions of I, II and III in 2:1 sulfuric acid are reported and compared. In addition, the effects of changes in reaction medium upon the transformations of I are noted.

Some time ago, Meyer, Meyer and Taeger[5] observed that the rearrangement of the tetrabromohydrazobenzene II occurs in 2:1 but not in 1:1 sulfuric acid and that concentrated sulfuric acid brings about disproportionation exclusively. Beyond establishing the presence of two primary amino groups in each of the two rearrangement products which they isolated, they attempted



XIII



XIV

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(1) This paper has been abstracted from a thesis submitted by William O. Forshey, Jr., to the Committee on Graduate Degrees, Carnegie Institute of Technology, in partial fulfillment of the requirements for the D. Sc. degree.

(2) Presented in part before the Organic Division of the American Chemical Society, New York, N. Y., September, 1947, and Chicago, Ill., April, 1948.

(3) Institute Graduate Fellow in Organic Chemistry, 1946-1948. Present address: Chemical Department, Experimental Station, E. I. du Pont de Nemours and Co., Wilmington, Delaware.

(4) Carlin, THIS JOURNAL, **67**, 928 (1945).

(5) Meyer, Meyer and Taeger, *Ber.*, **53**, 2034 (1920).