Intensities of the *h0l* reflections from crystals of the most pure preparation of each compound were slightly different. It was thought that the difference might be due to impurities. Diffraction patterns of the products in various stages of purification showed that impurities did indeed affect the intensities, but that the difference between the patterns of the most pure preparations could not be explained in terms of impurities present during preparation.

The condensations of 2-nitrofluorenone and 2-nitrofluorene with *p*-aminoethylbenzene and *p*-nitrosoethylbenzene, respectively, were undertaken because the products, if N-arylazomethines, would be the closest analogs of the *p*-methyl derivatives. However, in this case the nitroso condensation yielded a nitrone instead of an anil.

Both differently colored N-(2,5-dinitrofluorenylidene)-*p*-fluoroaniline products absorbed at 227 mμ (ϵ_{max} 33.2 × 10^3) and at 279 mμ (ϵ_{max} 26.1 × 10^3). Shoulders occurred at 315 mμ (ϵ_{max} 10.7 × 10^3) and at 337 mμ (ϵ_{max} 9.47 × 10^3).

The specific refractive index increments for the yellow form were 0.216, 0.213 and 0.223 (av. 0.217) for the 1.00% 0.50% and 0.25% solutions, respectively, and for the red form they were 0.215, 0.213 and 0.213 (av. 0.214).

A comparison of the infrared spectra of the two compounds in Nujol mulls showed bands at 1556 and 1369 cm.$^{-1}$ in the spectrum of the yellow compound which were absent in the other spectrum. Bands in the yellow spectrum at 1219 and 1228 cm.$^{-1}$ are replaced by one band at 1223 cm.$^{-1}$ in the spectrum of the red compound. The greater number of absorption bands in the spectrum of the yellow compound indicates a lesser degree of crystalline order and a lower stability. It is noteworthy that both forms of this substance exhibit identical spectra in postassium bromide disks. Apparently one or both forms changed when subjected to the pressure necessary to form the disk. It would appear that one cannot always distinguish between polymorphs by the potassium bromide pellet method.

Although the two N-(2,5-dinitrofluorenylidene)-*p*-fluoroaniline compounds are markedly different in color and gross crystalline structure, the two forms are identical in solution. The infrared spectra of their Nujol mulls are dissimilar, indicating that these forms are polymorphs rather than isomers.

Acknowledgments.—The authors wish to acknowledge their debt to Dr. L. H. Jensen, of the Department of Anatomy, University of Washington, for instruction, help and advice with the X-ray crystallography, and thank Drs. H. Neurath and W. B. Dandliker, of the Department of Biochemistry, University of Washington, for making the infrared spectrophotometer and the differential refractometer available for our use.

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[CONTRIBUTION FROM THE FRUIT AND VEGETABLE CHEMISTRY LABORATORY, WESTERN UTILIZATION RESEARCH AND DEVELOPMENT DIVISION, AGRICULTURAL RESEARCH SERVICE, UNITED STATES DEPARTMENT OF AGRICULTURE]

Plant Polyphenols. III. The Isolation of a New Ellagitannin from the Pellicle of the Walnut

BY LEONARD JURD[1]

RECEIVED NOVEMBER 18, 1957

The major constituent of the tannin from the walnut pellicle has been isolated. Analyses of numerous derivatives of the compound, for which the name *juglanin* is proposed, show that its molecular formula is $C_{27}H_{22}O_{18}$ and that it contains eleven hydroxyl groups. Acid and alkaline hydrolyses of juglanin give ellagic acid (I), gallic acid and glucose. The yields of these hydrolysis products and the analytical data indicate that juglanin is a polyphenol formed by the esterification of three hydroxyl groups of glucose with a molecule of gallic acid and a molecule of hexahydroxydiphenic acid (II). It is therefore isomeric with corilagin, but differs in the position of attachment of the galloyl and/or hexahydroxydiphenoyl units to glucose.

The isolation of ellagic acid, gallic acid, methyl gallate and a mixture of ellagitannins from the pellicle (skin) of the walnut has been previously reported.[2] Complex mixtures of ellagitannins frequently occur in plants. However, much of the earlier work on the structures of these substances is of doubtful value because of the difficulties encountered in the separation of individual constituents from the tannin mixtures and the lack of reliable methods for determining the purity of the isolated compounds. Thus little progress in the structural chemistry of ellagitannins was made until the recent work of Schmidt and his co-workers on the isolation and chemistry of corilagin[3-5] and chebulagic acid[6,7] from commercial myrobalans and divi-divi.

Two-dimensional chromatograms of the crude walnut tannin show that it contains at least ten polyphenols. Visual examination of the intensity of the spots in the developed chromatograms indicates that the polyphenol mixture consists chiefly of one major constituent (Table I, A) and smaller quantities of three other components (B,D,E). The high R_f value of A in water and the somewhat higher R_f values of B, C and D in organic solvents suggested the possibility of the selective removal of the latter components from aqueous solutions of

(1) Financial support for this work was provided by the Diamond Walnut Growers, Inc.

(2) L. Jurd, THIS JOURNAL, **78**, 3445 (1956).

(3) O. T. Schmidt and R. Lademann, *Ann.*, **571**, 232 (1951).

(4) O. T. Schmidt and D. M. Schmidt, *ibid.*, **578**, 31 (1952).

(5) O. T. Schmidt, D. M. Schmidt and J. Herok, *ibid.*, **587**, 67 (1954).

(6) O. T. Schmidt and W. Nieswandt, *ibid.*, **568**, 165 (1950).

(7) O. T. Schmidt and R. Lademann, *ibid.*, **569**, 149 (1950).

the tannin by extraction with organic solvents. It has been found that long extraction of an aqueous solution of the tannin with ethyl acetate preferentially removes B, C and D and related minor constituents with similar R_f values. The residual aqueous layer becomes relatively richer in A. Saturation of the aqueous layer with salt and re-extraction for a short time with ethyl acetate removes E and the last traces of B, C and D. Chromatograms of the aqueous salt solution then show only the presence of A and traces of minor polyphenols with similar R_f values. Compound A is isolated from the salt solution by long extraction with ethyl acetate. Addition of hexane to the ethyl acetate extract precipitates A as a cream colored, amorphous powder, m.p. 235–237°. It is proposed to name this ellagitannin juglanin. The juglanin thus obtained is essentially chromatographically pure although heavily loaded chromatograms do show the presence of minute amounts of two other polyphenols.

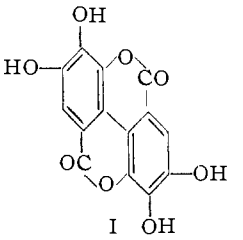
TABLE I

R_f VALUES OF POLYPHENOLIC CONSTITUENTS OF WALNUT TANNIN

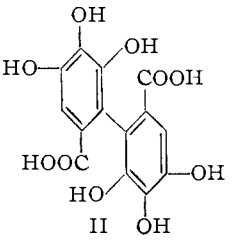
Compound	10% aqueous acetic acid, R_f	1-Butanol–acetic acid–water (4:1:5), R_f
A	0.63	0.38
B	.50	.53
C	.67	.60
D	.45	.47
E	.44	.40
F	.34	.34
G	.45	.21
H	.67	.21
I	.78	.35
Corilagin	.53	.46

Juglanin exhibits typical tannin reactions. Thus it precipitates gelatin from aqueous solution and gives an intense blue-black ferric reaction. Elementary analysis establishes its molecular formula as $C_{27}H_{22}O_{18}$. On acetylation and benzoylation it gives an amorphous acetate, $C_{49}H_{44}O_{29}$, and benzoate, $C_{104}H_{66}O_{29}$, respectively, each of which contains eleven acyl groups. Eleven of the eighteen oxygen atoms in juglanin therefore occur as free hydroxyl groups. Methylation of juglanin with diazomethane gives an amorphous methyl ether, $C_{37}H_{42}O_{18}$, containing ten methoxyl groups. In confirmation of this the methyl ether forms a monoacetate, $C_{39}H_{44}O_{19}$, and a mono-*p*-nitrobenzoate, $C_{44}H_{45}O_{21}N$, when acetylated and *p*-nitrobenzoylated, respectively. At least one of the eleven hydroxyls of juglanin is therefore an alcoholic hydroxyl group. The quantitative hydrolysis of juglanin in aqueous sulfuric acid gives 46.1% of its weight as ellagic acid, 7.8% as gallic acid and 17.0% as glucose. Alkaline hydrolysis of juglanin in an inert atmosphere gives a higher yield (12.9%) of gallic acid. Ellagic acid is a stable and easily isolable substance. The low yields of gallic acid and glucose, on the other hand, probably result from some decomposition of these substances during the hydrolysis.

Ellagic acid is not present as the lactone I in tannins. It occurs as the hexahydroxydiphenic acid (II). On hydrolysis of the tannin the liberated hexahydroxydiphenic acid lactonizes to ellagic acid (I).[8] The esterification of three of the hydroxyl groups of glucose by one molecule of hexahydroxydiphenic acid and one molecule of gallic acid would result in the formation of a polyphenol ester, $C_{27}H_{22}O_{18}$. This compound contains eleven hydroxyl groups and on hydrolysis should give 47.6% ellagic acid, 28.4% gallic acid and 28.4% glucose. The analytical and hydrolytic data obtained for juglanin are thus in general agreement with the data to be expected for this combination of hexahydroxydiphenic acid, gallic acid and glucose.

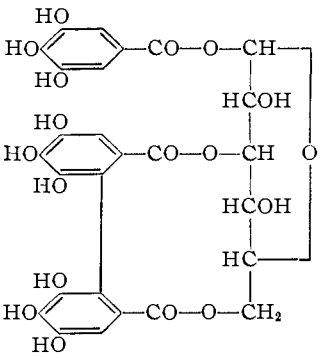


I



II

Corilagin has the molecular formula $C_{27}H_{22}O_{18}$, contains eleven hydroxyl groups, and has the constitution III.[3,5]



III

Jug nin is therefore isomeric with, and structurally similar to, corilagin. The melting point (m.p. 235–237°), optical rotation ($[\alpha]^{20}D$ +52.0°) and R_f values of juglanin, however, differ markedly from those of corilagin[9] (m.p. 204–205°, $[\alpha]^{20}D$ −228°). A two dimensional co-chromatogram of juglanin and corilagin shows two distinct spots. Furthermore corilagin reacts with diazomethane to form a enneamethyl ether. Juglanin, on the other hand, gives a decamethyl ether, indicating that it contains a fairly acidic alcoholic hydroxyl group. Juglanin differs from corilagin, therefore, in the positions of the linkages of the galloyl- and/or hexahydroxydiphenoyl- units to glucose. Further work to establish the location of these units is in progress.

Experimental

Because of the amorphous nature of juglanin derivatives and their indefinite melting points, each of the derivatives was prepared at least twice from juglanin. The analytical data for the product obtained in each of these preparative reactions are reported.

(8) O. T. Schmidt, F. Blinn and R. Lademann, *Ann.*, **576**, 75 (1952).

(9) For chromatographic comparison a specimen of Dr. O. Schmidt's authentic corilagin was kindly supplied by Dr. H. G. C. King.

Isolation of the Crude Tannin from the Walnut Pellicle.—A method for the isolation of the crude tannin (tannin fractions A and B) from methanolic extracts of the pellicle has been described.[2] It was later found that acetone extraction of the pellicle gave a product less contaminated with carbohydrate and other materials. The acetone extract was worked up exactly as described for the methanol extract and gave approximately the same yields of crude tannin. Chromatograms of tannin fractions A and B showed that each contained the same phenolic constituents although in slightly different relative amounts. Tannin fraction A also contained free carbohydrate. For the isolation of juglanin tannin fractions A and B were combined.

Isolation of Juglanin from the Tannin.—A solution of the tannin (85.0 g.) in water (850 ml.) was extracted with ethyl acetate in a continuous liquid–liquid extractor for 6 hours (ethyl acetate extract 1). Fresh ethyl acetate was added and the extraction was continued for 16 hours (extract 2). The aqueous solution was saturated with sodium chloride. An oily material (3) was precipitated and collected. The aqueous salt solution was then extracted with ethyl acetate for 18 hours (extract 4). Three more ethyl acetate extractions, each for 24 hours, were made, giving extracts 5, 6, 7.

Each of the ethyl acetate extracts was dried (Na_2SO_4), concentrated to smaller volume, and added to excess of warm hexane. The tannin in each extract was thereby precipitated as an amorphous powder. This was collected, washed thoroughly with hexane and dried at 100°. The recovery of solid from each extract was as follows: 1, 7.9 g.; 2, 9.3 g.; 3, 9.5 g.; 4, 16.1 g.; 5, 6.4 g.; 6, 4.8 g.; 7, 1.1 g. Two-dimensional chromatograms of fractions 5, 6 and 7 showed that these consisted of juglanin with only traces of two minor polyphenols (Table I, A). Fractions 3 and 4 were rich in juglanin but contained appreciable quantities of the other polyphenols. Fractions 1 and 2 contained little juglanin and were rich in the other major tannin components (Table I, B, C, D).

Juglanin.—Juglanin, reprecipitated six times from ethyl acetate–hexane, was obtained as a cream, amorphous powder, m.p. 235–237° dec., $[\alpha]^{20}D$ +52.0° (*c* 0.50 in water). It gave precipitates with aqueous gelatin and lead acetate solutions and a deep blue-black color with alcoholic ferric chloride.

Anal. Calcd. for $C_{27}H_{22}O_{18}$: C, 51.1; H, 3.58. Found: C, 51.1; H, 3.55.

Undecaacetyljuglanin.—A mixture of juglanin (0.1 g.), acetic anhydride (0.5 ml.) and fused sodium acetate (0.1 g.) was heated to boiling for 0.5 minute and then placed in a steam-bath for 10 minutes. Excess of water was added to the cooled solution. When the excess of acetic anhydride was hydrolyzed the semi-solid product was extracted with ethyl acetate (20 ml.). The ethyl acetate extract was washed with water, dried (Na_2SO_4) and diluted with hexane (40 ml.). The precipitated acetate was collected and dissolved in a small volume of warm methanol. On cooling the acetate separated as an amorphous solid. It was reprecipitated from methanol and again from ethyl acetate–hexane for analysis. Undecaacetyljuglanin was thus obtained as an amorphous, white powder, m.p. 237–241°. It did not dissolve in cold aqueous sodium hydroxide and did not give a ferric chloride reaction.

Anal. Calcd. for $C_{49}H_{44}O_{29}$: C, 53.6; H, 4.04; 11 CH_3CO–, 43.2. Found: (1) C, 53.7; H, 3.97. (2) C, 53.7; H, 3.87; CH_3CO–, 42.0.

Undecabenzoyljuglanin.—A solution of juglanin (0.15 g.) and benzoyl chloride (0.2 ml.) in pyridine (1.0 ml.) was allowed to stand at 0° for 20 hours and then added to water. The solid product was collected, washed well with aqueous sodium bicarbonate and with water, and dissolved in warm acetone. Methanol was added and the solution was concentrated until an oily product began to separate. On cooling the oil solidified. It was collected and reprecipitated twice more from methanol–acetone. For analysis it was finally precipitated from ethyl acetate by the addition of hexane. Undecabenzoyljuglanin separated as a colorless, amorphous solid, m.p. 215–217°, which did not give a ferric test.

Anal. Calcd. for $C_{104}H_{66}O_{29}$: C, 70.2; H, 3.74. Found: (1) C, 69.8; H, 3.69; (2) C, 69.8; H, 3.71.

Decamethyljuglanin.—Excess of an ethereal solution of diazomethane was added to a solution of juglanin (0.4 g.) in methanol (10.0 ml.). After standing for 20 hours the solution was evaporated to a gum. This was dissolved in ethyl acetate. Addition of hexane to the solution precipitated the methyl ether as an amorphous solid. This was reprecipitated twice from aqueous methanol and again from ethyl acetate–hexane. The decamethyl ether was obtained as an amorphous, slightly yellow solid which softened at 150–153° and melted at 157–165°. It did not dissolve in aqueous alkali and did not give a ferric reaction.

Anal. Calcd. for $C_{37}H_{42}O_{18}$: C, 57.3; H, 5.47; 10 MeO–, 40.3. Found: (1) C, 57.5; H, 5.30; MeO–, 39.3; (2) C, 57.6; H, 5.31; MeO–, 39.1.

Decamethyljuglanin Monoacetate.—Decamethyljuglanin (0.15 g.) was boiled with acetic anhydride (0.5 ml.) and fused sodium acetate (0.2 g.) for one minute. The cooled solution was added to excess of water and the precipitated gum was extracted with ethyl acetate. Addition of hexane to the dried (Na_2SO_4) ethyl acetate solution precipitated the acetate as an amorphous solid. It was reprecipitated from aqueous methanol and from ethyl acetate–hexane. Decamethyljuglanin monoacetate separated as an amorphous, colorless powder, m.p. 142–145°.

Anal. Calcd. for $C_{39}H_{44}O_{19}$: C, 57.3; H, 5.43; 10 MeO–, 38.2; 1 CH_3CO–, 5.29. Found: (1) C, 57.5; H, 5.08; MeO–, 36.2; CH_3CO–, 5.53; (2) C, 57.4; H, 5.46; MeO–, 37.4; CH_3CO–, 5.79.

Decamethyljuglanin Mono-*p*-nitrobenzoate.—A solution of *p*-nitrobenzoyl chloride (0.2 g.) and decamethyljuglanin (75 mg.) in pyridine (0.2 ml.) was maintained at 0° for 20 hours. After the addition of water the product was collected, washed thoroughly with aqueous sodium bicarbonate, and dissolved in warm methanol. Water was added dropwise until the solution became cloudy. The *p*-nitrobenzoate separated as a slightly brown solid on standing. The product was reprecipitated three times for analysis. The *p*-nitrobenzoate was obtained as an amorphous, slightly brown powder, m.p. 156–158°.

Anal. Calcd. for $C_{44}H_{45}O_{21}N$: C, 57.2; H, 4.91; N, 1.52. Found: C, 57.6; H, 4.93; N, 1.70.

Quantitative Acid Hydrolysis of Juglanin.—A solution of juglanin (1.887 g.) in 5% aqueous sulfuric acid (20.0 ml.) was heated under reflux on a steam-bath for 22 hours, cooled to 0° for 2 hours and filtered. The crystalline product was washed with warm water and with acetone (3 × 5.0 ml.) and dried at 100° (A, ellagic acid) (0.870 g., 46.1%). The washings from A were combined with the aqueous acid filtrate and the solution was concentrated to about 20 ml. when a dark tar separated. The hot aqueous solution was decanted from the tar which, after washing with a little warm water and ether, was discarded. The aqueous solution, combined with the water and ether washings of the tar, was extracted with ether for 7 hours in a continuous liquid–liquid extractor. The ether extract, filtered from a small quantity of crystalline ellagic acid (0.041 g.) which separated, was evaporated to a gum (B, gallic acid) (0.1473 g., 7.8%). The aqueous sulfuric acid layer was filtered through talcum and treated with excess of aqueous lead acetate to precipitate lead sulfate and the lead salts of any remaining phenols. The filtrate from the lead salts was treated with hydrogen sulfide. The precipitated lead sulfide was removed by filtration through Celite. The colorless aqueous filtrate was concentrated to exactly 25.0 ml. and the optical rotation of the solution was determined; α = +0.67°, corresponding to 17.0% glucose.[3] The aqueous solution was then concentrated to 10 ml. and phenylhydrazine hydrochloride (0.8 g.) and sodium acetate (1.2 g.) were added. The solution was heated in a boiling water-bath for 45 minutes, cooled, and filtered. The yellow osazone (0.259 g.) was recrystallized from methanol. It separated in yellow needles, m.p. 202°, undepressed on admixture with authentic glucosazone.

For the purpose of identification A was recrystallized from aqueous pyridine and from methanol–acetone. It was obtained as yellow needles, m.p. >360°. Its ultraviolet spectra in ethanol and in ethanolic sodium acetate had λ_{max} 365, 256 and λ_{max} 355, 277, 256, respectively. On Whatman No. 1 paper it had R_f 0 in water and R_f 0.33 in 1-butanol–acetic acid–water. On paper chromatograms it exhibited a bright blue fluorescence in ultraviolet light, changing to a yellow-green with ammonia vapor. The m.p., spectra and R_f values[2] of synthetic ellagic acid were identical with those of A.

Compound D was identified as gallic acid chromatographically and spectrally. Paper chromatograms of D showed a weak ellagic acid spot and an intense spot whose R_f values were identical with those of gallic acid (R_f 0.50 in 10% aqueous acetic acid; R_f 0.74 in 1-butanol–acetic acid–water. Two-dimensional co-chromatograms of D and authentic gallic acid in these solvents showed only one major spot. The spectrum of the intense spot in a two-dimensional chromatogram of A was determined directly on the paper strip.[10] It had λ_{max} 279 mμ. After dipping it into alcoholic sodium acetate and drying it had λ_{max} 264 mμ. Gallic acid, similarly chromatographed, had λ_{max} 278 and 263 mμ, respectively.

Alkaline Hydrolysis of Juglanin.—Aqueous sodium hydroxide (50.0 ml., 10%) was added to a solution of juglanin (5.0 g.) in water (50.0 ml.) under an atmosphere of nitrogen. The stoppered reaction flask was allowed to stand at room temperature for 5 days during which time a yellow sodium salt crystallized. The sodium salt was collected, suspended in warm water and treated with excess of hydrochloric acid. Ellagic acid, m.p. >360°, was thereby obtained (1.7 g., 34%). After removal of the sodium ellagate, the sodium hydroxide filtrate was acidified with dilute sulfuric acid. A dark tar was precipitated. The aqueous acid solution was decanted from the tar and extracted with ether for 6 hours in a continuous liquid–liquid extractor. The ether extract was dried (Na_2SO_4) and evaporated. A slightly brown, crystalline solid, identified chromatographically and spectrally as gallic acid, was obtained (0.645 g., 12.9%). Recrystallized from water the product had m.p. 258–259°, undepressed on admixture with gallic acid.

Acknowledgments.—The author is indebted to L. M. White for the elementary analyses.

PASADENA, CALIF.

(10) A. E. Bradfield and A. E. Flood, *J. Chem. Soc.*, 4740 (1952).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OHIO UNIVERSITY]

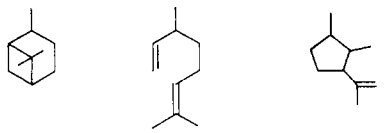
Reactions of Diolefins at High Temperatures. I. Kinetics of the Cyclization of 3,7-Dimethyl-1,6-octadiene[1]

BY WILLIAM D. HUNTSMAN AND THOMAS H. CURRY

RECEIVED NOVEMBER 14, 1957

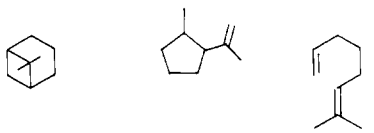
The cyclization of 3,7-dimethyl-1,6-octadiene at 382.5° and 409° is first-order, and the rate is not affected by the presence of nitric oxide or ethylene oxide. The Arrhenius energy of activation is 35.2 kcal./mole and the entropy of activation is −18 e.u. An intramolecular mechanism is proposed.

Pinane (I) isomerizes at 450–500° to give a mixture of 3,7-dimethyl-1,6-octadiene (II) and 1,2-dimethyl-3-isopropenylcyclopentane (III).[2,3] Furthermore, it has been shown that III arises by



I II III

cyclization of II. Under similar conditions, 6,6-dimethylnorpinane (IV) isomerizes to 1-methyl-2-isopropenylcyclopentane (V), presumably *via* 7-methyl-1,6-octadiene (VI).[4]



IV V VI

It was suggested that the cyclization step in these reactions proceeds by a free radical chain mechanism. Several points, however, argue against such a mechanism. Among them may be mentioned the virtual absence of polymeric products. Also the reactions are surprisingly specific as compared with most hydrocarbon–pyrolysis reactions. One would expect a much more complex mixture if a radical chain mechanism were operative.[5]

It was felt that the cyclization of 1,6-diolefins warranted further study, with the particular goal of substantiating or ruling out a free radical chain mechanism. Accordingly, an investigation of the kinetics of cyclization of 3,7-dimethyl-1,6-octadiene was undertaken.

Several preliminary experiments were conducted to gain an estimate of the effect of free radical chain initiators. The results of some of these experiments are summarized in Table I. *t*-Butyl peroxide and ethylene oxide have been widely used as initiators for reactions which occur by radical chain mechanisms. They are observed to accelerate reactions, and to induce reactions at temperatures where the reactants are normally stable. For example, *t*-butyl peroxide sensitizes the polymerization of olefins, and the decarbonylation of aldehydes[6]; ethylene oxide has been used as an initiator for the decomposition of alkanes, ethers and aldehydes.[7]

Inspection of Table I reveals that these initiators exerted little if any effect on the cyclization of II, the major effect being to increase the extent of polymerization. The small amount of cyclization observed in run 1 probably does not signify that the peroxide sensitized the cyclization reaction. Mixtures of II and III were used in these experiments

(1) This research was supported by the United States Air Force, through the Office of Scientific Research of the Air Research and Development command.

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(5) J. E. Leffler, "The Reactive Intermediates of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1956, p. 242.

(6) F. F. Rust, F. H. Seubold and W. E. Vaughan, THIS JOURNAL, **70**, 95, 4253 (1948); E. H. Farmer and C. G. Moore, *J. Chem. Soc.*, 131 (1951); R. N. Haward and W. Simpson, *Trans. Faraday Soc.*, **47**, 212 (1951).

(7) C. J. M. Fletcher, THIS JOURNAL, **58**, 534 (1936); C. J. M. Fletcher and G. K. Rollefson, *ibid.*, **58**, 2135 (1936); L. S. Echols and R. N. Pease, *ibid.*, **58**, 1317 (1936).