The identical product was also obtained as follows. The adduct to propylene formed in the lower yield, 0.75 g., m. p. 108–108.5° was oxidized to 0.45 g. (55% yield) of 2,4-dinitrophenyl 1′-methyl-2′-chloroethyl sulfone, m. p. 97–97.5°.

Anal. Calcd. for $C_9H_9N_2O_6SCl$: C, 35.01; H, 2.94. Found: C, 35.02; H, 3.00.

The latter product, 0.354 g., was dehydrochlorinated with triethylamine (dried by distillation from potassium hydroxide), yielding 0.22 g. (71%) of 2,4-dinitrophenyl isopropenyl sulfone, m. p. 129–129.5° (recrystallized from carbon tetrachloride).

Anal. Calcd. for $C_9H_8N_2O_6S$: C, 39.71; H, 2.96. Found: C, 40.10; H, 3.01.

The 2,4-dinitrophenyl *iso*propenyl sulfone (0.120 g.) was hydrogenated, then benzoylated, yielding 0.158 g. (85%) of a slightly colored product which melted at 204–206°. Repeated treatment with activated charcoal in ethyl alcohol resulted in colorless crystals. These melted at 212–213°, and showed no depression in a mixed melting point determination with the 2,4-dibenzamidophenyl isopropyl sulfone obtained by the alternate route from 2,4-dinitrophenyl isopropyl sulfide.

Effect of Peroxides.—A solution of 0.45 g. of 2,4-dinitrobenzenesulfenyl chloride, 0.02 g. of dibenzoyl peroxide, and 1 ml. of styrene in 10 ml. of benzene was allowed to stand for four hours and then concentrated by evaporation with an air-stream. The yellow solid which separated was recrystallized from benzene, dried, and found to melt at 141–142°. It did not depress the melting point of the adduct to styrene obtained in the absence of peroxides.

The percentage of the two adducts to propylene, using 1.00 g. of 2,4-dinitrobenzenesulfenyl chloride in glacial acetic acid, was not noticeably affected by the presence of 0.03 g. of benzoyl peroxide. The addition to propylene in carbon tetrachloride was not completely effected in two weeks either in the presence or in the absence of benzoyl peroxide or acetyl peroxide.

In the above experiments, the amounts of peroxides employed were not sufficient to permit recovery of the suspected product of the oxidation of 2,4-dinitrobenzenesulfenyl chloride. That the peroxide oxidizes the reagent to 2,4-dinitrobenzenesulfonyl chloride was shown by permitting a solution of 0.10 g. of 2,4-dinitrobenzenesulfenyl chloride and 0.30 g. of benzoyl peroxide, in 10 ml. of carbon tetrachloride, to stand at room temperature for four hours. On concentrating the solution in an air-stream, 2,4-dinitrobenzenesulfonyl chloride separated in nearly colorless crystals, m. p. 101–102°. The reported value for this compound is 102°.[10]

Acknowledgment.—We are indebted to the Abbott Laboratories of North Chicago, Illinois, for a fellowship grant in support of this work. The microanalyses for carbon and hydrogen were performed by the late Dr. Gertrud Oppenheimer.

Summary

2,4-Dinitrobenzenesulfenyl chloride promises to be a most versatile reagent for the characterization of various classes of organic compounds. The present study reports the characterization of a series of olefins with this reagent.

The additions of 2,4-dinitrobenzenesulfenyl chloride to symmetrical olefins or negatively substituted olefins, such as styrene, yield single adducts. Other olefins, such as propylene and pentene-2, yield mixtures of isomeric adducts. Of the two isomeric adducts to propylene, the product isolated in 65% yield was proved to be the one predictable by Markownikoff's rule. The structure of the other isomer (isolated in 15% yield) was also established in an unambiguous manner.

In a few instances, as with 1,1-diphenylethylene, addition of the reagent is accompanied by dehydrohalogenation, yielding vinyl sulfides rather than the usually observed β-chloro sulfides.

The presence of peroxides was found not to affect the mode of addition to propylene or styrene. Benzoyl peroxide oxidizes 2,4-dinitrobenzenesulfenyl chloride to 2,4-dinitrobenzenesulfonyl chloride.

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(10) J. M. Sprague and T. B. Johnson, THIS JOURNAL, **59**, 2439 (1937).

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF DELAWARE]

Polymerization of Fatty Acid Esters of 3-Butene-1,2-diol. I.[1]

BY ELIZABETH DYER, THOMAS G. CUSTER[2] AND WILLIAM C. MEISENHELDER[3]

The formation of polymers from the higher fatty acid esters of monohydric unsaturated alcohols, such as vinyl, allyl, and substituted allyl, has been reported,[4,5,6,7] but there is no published work on the polymerization of such esters of a dihydric unsaturated alcohol. In this paper a report is made of the polymerization of the acetic and palmitic esters of the unsaturated glycol 3-butene-1,2-diol (erythrol). A study of the oleic and linoleic esters of erythrol is in progress. Erythrol is obtainable through hydrolysis of 3,4-epoxy-1-butene[8] (butadiene monoxide).

Erythryl dipalmitate and diacetate were most conveniently obtained by the reactions of the corresponding acid chloride with erythrol in pyridine. The diacetate was previously prepared by Henninger[9] from erythrol and acetic anhydride, the dipalmitate from the successive reactions of butadiene monoxide with one equivalent of palmitic acid in the presence of ferric chloride and with one equivalent of palmitoyl chloride.[10]

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[1] From the Master's Theses of Thomas G. Custer and William C. Meisenhelder, University of Delaware, 1948.

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[4] Powers, *Ind. Eng. Chem.*, **38**, 837 (1946).

[5] Dean, U. S. Patent 2,374,081, April 17, 1945.

[6] Swern, Billen and Knight, THIS JOURNAL, **69**, 2439 (1947).

[7] Swern and Jordan, *ibid.* **70**, 2334 (1948).

[8] Pariselle, *Ann. chim. phys.*, [8] **24**, 392 (1911).

[9] Henninger, *ibid.*, [6] **7**, 214 (1886).

[10] Unpublished work of Whitmore and Krems, Brooklyn Polytechnic Institute.

Attempts to polymerize the esters in emulsion proved unpromising. The erythryl dipalmitate did not self-polymerize at 40° in the presence of potassium persulfate although it formed an emulsion copolymer with styrene, which contained one ester unit per twenty-four styrene units. By the use of bulk polymerization, on the other hand, self-polymers and copolymers were obtained from erythryl diacetate and dipalmitate. The possibility that these products were merely polystyrene contaminated with monomeric ester was excluded by repeated precipitations from solvent mixtures in which the monomers were soluble. A summary of the data on the polymers is given in Table I.

TABLE I

POLYMERIZATION OF ERYTHRYL ESTERS AT 80° WITH 4% BY WEIGHT OF BENZOYL PEROXIDE

Ester in monomers, %	Yield[a] of polymer, %	Polymer analyses[b] I. V.	Polymer analyses[b] Sapn. no.	Moles styrene/mole ester in copolymer from sapn. no.	Approx. molecular weight
		Erythryl Diacetate and Styrene			
100	20	2.30	677[c]		3900[g]
100	36	1.46	687		2200[g]
62[e]	20	2.22	44.9	22	
50	40	3.66	57.7	17	
		Erythryl Dipalmitate and Styrene			
100	84	19.1			980[d,h]
85[e]	11		50.1	16	
85[e]	11	4.41	59.5	13	
70	16	2.74	36.4	24	15000[i]
50	35	2.88	23.9	40	
50	42	2.65	19.4	50	
30	66	2.37	21.9	44	19700[i]
0[f]	84	2.25	12.3		

[a] Based on total monomers. [b] Average values. [c] Theoretical, 652. [d] The value 980 could represent a mixture of dimer and monomer containing 74% dimer. [e] An approximately equimolar mixture of ester and styrene. [f] Styrene control. [g] Rast method in camphor. [h] Cryoscopic in cyclohexane. [i] Viscosity average in benzene.

The results show that when erythryl diacetate was heated at 80° in the presence of benzoyl peroxide (4% of the monomer weight), a polymer was formed which had an average degree of polymerization of 18. Bartlett and Altschul[11] found that allyl acetate under similar conditions yielded a product with a degree of polymerization of 13. Thus it would appear that erythryl diacetate resembles allyl acetate in polymerizability. Bartlett and Altschul also proved the presence in their polymers of benzoate radicals from the catalyst. The high saponification values of the polymeric erythryl diacetate (677 and 687 instead of 652) might be due to benzoate groups which had become attached to the allylic double bond during the initiation or termination of the polymerization reaction.

The erythryl dipalmitate under the same conditions yielded a product which was shown by the iodine value and molecular weight to be largely a dimer.

The molar composition of the copolymers was calculated from the saponification numbers. The copolymer ratios are probably in error by an unknown amount which represents acidic groups, other than fatty acid radicals, since the polystyrene controls gave appreciable saponification numbers. This acidity is not due to free acid, as the acid numbers of all the polymers were negligible. It is probably caused by benzoate groups from the catalyst.

It is apparent from Table I that a decrease in the ester content of the monomer mixture produced a decrease in the proportion of erythryl dipalmitate in the copolymer. It was not possible to calculate precise monomer reactivity ratios[12] because of the uncertainty in the absolute values of the copolymer compositions, as well as the fact that the yields were not determined until after numerous reprecipitations.

The copolymers had relatively low molecular weights, which were slightly increased by decreasing the per cent. of ester in the monomer mixture from 70 to 30. The dipalmitate copolymers of molecular weights 15,000 and 19,700 contained five and four ester groups, respectively, per chain.

The physical properties of the copolymers also varied with the composition of the monomer mixture, as shown in Table II. As the per cent. of ester in the monomer mixture was decreased, the initial softening temperature rose and the solubility in acetone or in solvents common to all decreased. Like polystyrene, all the polymers were soluble in benzene, dioxane and chloroform, insoluble in water, methanol, ethanol, acetic acid and petroleum ether.

TABLE II

PROPERTIES OF COPOLYMERS OF ERYTHRYL DIACETATE AND ERYTHRYL DIPALMITATE WITH STYRENE

Ester in monomers, %	Melting range,[a] °C. Diacet.	Melting range,[a] °C. Dipalm.	Solubility in acetone[b] Diacet.	Solubility in acetone[b] Dipalm.
100	65–89	41–54	S	PS
85		85–200		PS
70		93–>140		SO
62	110–140[d]		S	
50	110–150[d]	108–>250	S	PS
30		115–>240		PS
0[c]	140–>250		SW	

[a] Temperature of initial softening to complete fluidity. [b] S = completely soluble, solution clear. SO = soluble, but solution opaque. PS = partially soluble. SW = swelling. [c] Polystrene control. [d] With decomposition

Experimental

3-Butene-1,2-diol (Erythrol).—This substance was prepared by the acid-catalyzed hydrolysis of butadiene mon-

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(11) Bartlett and Altschul, THIS JOURNAL, **67**, 816 (1945).

(12) Mayo and Lewis, *ibid.*, **66**, 1594 (1944).

oxide[13] according to the method of Pariselle.[8] The product, obtained in yields of 42 to 60%, boiled in the range 71–95° at pressures varying from 2–11 mm., and had iodine values of 280–287 (theoretical 288).

Dipalmitate of 3-Butene-1,2-diol (Erythryl Dipalmitate).—To a solution of 16.5 g. (0.06 mole) of palmitoyl chloride (prepared by the method of Bauer[14] from Eastman Kodak Co. palmitic acid, m. p. 61–62°) in 125 ml. of petroleum ether was added slowly during cooling and stirring 6.3 g. (0.08 mole) of pyridine and then 2.7 g. (0.03 mole) of erythrol. After refluxing on a water-bath for two to three hours, the mixture was cooled, treated with 50 ml. of water, 50 ml. of 6 *M* hydrochloric acid and 150 ml. of petroleum ether. The layers were separated, the ether solution was washed with water, cold dilute alkali, and saturated salt solution until neutral, dried over anhydrous sodium sulfate, and the solvent removed under reduced pressure. The product consisted of 13 g. (76% yield) of a solid. After recrystallization to constant melting point from methanol the ester was a white material which softened and flowed at 32°, and became a clear liquid at 46–48°. It was easily soluble in benzene, chloroform, petroleum ether, acetone, hot ethanol, and hot methanol.

Anal. Calcd. iodine value, 44.8; saponification number, 199; acid number, 0. Found: iodine value, 44.1; saponification number 208; acid number, 0.

Diacetate of 3-Butene-1,2-diol (Erythryl Diacetate).—This ester,[9] prepared in yields of 43 to 53% from acetyl chloride and erythrol by the procedure described above for the dipalmitate, is a colorless liquid boiling at 203–204°. It was insoluble in water and soluble in acetone, alcohol, benzene, petroleum ether, and ether.

Anal. Calcd.: I. V., 146; sapn. no., 648; acid no., 0. Found: I. V., 145; sapn. no., 633; acid no., 0.

Polymerizations. A. Emulsion.—The erythryl dipalmitate formed no polymer by itself, but gave a 19% yield of a copolymer with styrene when a mixture of 5 g. of the ester, 5 g. of styrene (purified by alkaline washing and distillation under reduced pressure immediately before use), 1.0 g. of sodium oleate, 0.06 g. of potassium persulfate and 43 ml. of water was heated under nitrogen at 40° for twenty hours. This copolymer contained one ester unit per twenty-seven styrene units (sapn. no., 32.4).

B. Bulk.—Polymerizations were carried out on the esters alone and mixtures of each ester with styrene in varying proportions in the presence of benzoyl peroxide (4% of the total monomer weight). The mixtures were introduced into tubes which were evacuated, flushed with nitrogen, and heated for forty-four hours at 80°.

After the heating period the contents of the tubes were dissolved in benzene or chloroform, washed with cold 9% sodium carbonate to remove benzoyl peroxide and benzoic acid, then with saturated salt solution (or very dilute acid), and finally with water until neutral. The polymers were precipitated by slow addition of the benzene solution to methanol, followed by soaking of the precipitate in fresh non-solvent. All products were reprecipitated two or three times from solutions in benzene, chloroform, or dioxane by non-solvents such as ethanol, methanol, or petroleum ether. All of the polymers were eventually white powdery solids.

From the filtrates from the first precipitation monomeric esters were recovered in amounts varying from 52 to 87% of the quantities used. The lowered iodine values on these recovered esters (32–38 for the dipalmitate, theoretical 44) indicated that some loss of unsaturation had occurred, possibly due to oxidation by the benzoyl peroxide. Evaporation of the filtrates from the last precipitations yielded negligible residues, showing that the monomeric ester was completely removed.

Methods of Analysis.—Iodine values on the monomeric esters were conveniently secured by a catalytic modification[15] of the Wijs method. The polymers were analyzed for unsaturation by the use of the Woburn solution.[16]

Saponification numbers on erythryl dipalmitate were obtained by the Rieman[17] double indicator method, on erythryl diacetate and all polymers in the usual way with phenolphthalein. A Beckmann *p*H meter was used for the titrations. With the polymers the reagent used was 0.5 *N* potassium hydroxide in a 1:1 mixture of diethylene glycol and dioxane. Blanks were always run concurrently.

Viscosity measurements were made in an Ostwald viscosimeter in benzene solution at 25°. Intrinsic viscosities were determined by extrapolating to zero concentration the straight line plots of η_{sp}/c and of ln η_{rel}/c against the concentration, using solutions of four concentrations. Approximately the same values of intrinsic viscosity were obtained by the use of Smith's equation[18] with a single measurement at a concentration of 0.5 to 0.6 g. per 100 ml. Viscosity average molecular weights were calculated by Ewart's equation.[19]

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Summary

Bulk polymerization of erythryl diacetate at 80° with benzoyl peroxide (4% of the monomer weight) yielded a polymer which contained 13 to 23 monomer units. Under the same conditions erythryl dipalmitate was largely converted to a dimer.

Both esters formed copolymers with styrene which were relatively low in ester content and in molecular weight. The molar composition and physical properties of the copolymers varied with the composition of the monomer mixture.

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[13] Obtained through the courtesy of the Columbia Chemical Division of the Pittsburgh Plate Glass Company.

[14] Bauer, *Oil and Soap*, **23**, 1 (1946).

[15] Hoffman and Green, *Oil and Soap*, **16**, 236 (1939).

[16] Von Mikusch and Frazier, *Ind. Eng. Chem., Anal. Ed.*, **13**, 782 (1941).

[17] Rieman, *Ind. Eng. Chem., Anal. Ed.*, **15**, 325 (1943).

[18] Smith, THIS JOURNAL, **68**, 2061 (1946).

[19] Ewart, Tingey and Wales, unpublished work, referred to in Smith, *loc. cit.*