phorus pentachloride gave an exothermic reaction five minutes after mixing. Alternate cooling and shaking permitted control of the reaction, and the mixture was heated to 80° for ten minutes to complete the reaction. After an additional three hours at 25° (longer periods of time gave extensive carbonization), the mixture was washed with aqueous sodium bicarbonate and extracted with ether. Removal of the ether by evacuation and recrystallization of the crude product from cold ethanol–water gave 0.0049 mole (22.3%) of pentaerythritol chloride trinitrate, m.p. 60–62°. A further recrystallization from the same solvent gave m.p. 61–62°, mixed m.p. 63–64°.

Pentaerythritol Bromide Dinitrate.—3,3-Bis-(nitratomethyl)-oxetane, 8 g., was dissolved in acetone, 80 ml., and 48% hydrobromic acid, 48 g., was added slowly with stirring in ten minutes. The solution after standing for an additional ten minutes was added to 300 ml. of water and the organic layer separated and evacuated to give 8.15 g. (81.5%) of pentaerythritol bromide dinitrate, a liquid, $n^{30}D$ 1.5095.

Anal. Calcd. for $C_5H_9O_7N_2Br$: C, 20.77; H, 3.12; N, 9.69. Found: C, 21.17; H, 3.30; N, 9.36.

Pentaerythritol Bromide Trinitrate.—Pentaerythritol bromide dinitrate, 7.7 g., was added slowly with air agitation in 20 minutes to 30 g. of almost water-white 100% nitric acid at −5°. The air agitation was continued for 90 minutes at −5° and the reaction mixture then poured into ice and water. The precipitate was filtered and washed with water, 5% aqueous sodium bicarbonate and then water to give 8.2 g. (91%) of crude material. Recrystallization from hot ethanol gave white crystals, m.p. 89–90°.

Anal. Calcd. for $C_5H_8O_9N_3Br$: C, 17.97; H, 2.40; N, 12.58. Found: C, 18.30; H, 2.36; N, 12.58.

Pentaerythritol Iodide Trinitrate.—A solution of 2.00 g. of pentaerythritol bromide trinitrate, 1.00 g. of potassium iodide and 50 g. of anhydrous acetone was refluxed for two hundred hours. The potassium bromide was removed by filtration and the filtrate evaporated to give 0.92 g. (41%) of pentaerythritol iodide trinitrate, m.p. 108.5–110.5°. Shorter reaction times gave mixtures of the iodide and bromide.

Anal. Calcd. for $C_5H_8O_9N_3I$: C, 15.75; H, 2.10; N, 11.02. Found: C, 15.97; H, 2.19; N, 10.84.

Reactions of Halides of Pentaerythritol Trinitrate.—The following attempted reactions gave 70–100% recovery of the unreacted pentaerythritol halide trinitrate. In all cases the reaction mixture was refluxed for 40–120 hours: (1) pentaerythritol bromide trinitrate and silver nitrate in ethanol or acetonitrile, (2) pentaerythritol chloride trinitrate and silver nitrate in ethanol, (3) pentaerythritol bromide trinitrate and lead nitrate in ethanol, (4) pentaerythritol chloride trinitrate and potassium iodide in acetone and (5) pentaerythritol bromide trinitrate and silver cyanide in absolute ethanol.

The refluxing of a solution of pentaerythritol bromide trinitrate and sodium cyanide in 95% ethanol for five hours gave a 50% recovery of the halide and no other water-insoluble products. A similar reaction was obtained with sodium ethylate. With these reagents the pentaerythritol bromide trinitrate appeared to undergo alkaline hydrolytic reactions.

Hydrolysis of Pentaerythritol Trinitrate Halides.—To a solution of 0.8×10^{-3} mole of pentaerythritol chloride trinitrate in 40 ml. of acetone there was added a measured excess of standard sodium hydroxide. After one hour the solution was back-titrated with nitric acid, and it was found that 1.96×10^{-4} mole of sodium hydroxide had been consumed. The solution was ether extracted, and the aqueous layer on analysis for chloride ion by the silver chloride method gave a value of 4.1×10^{-5} mole. This indicated that equivalent quantities of nitrate and chloride groups had been hydrolyzed. The same procedure for pentaerythritol bromide trinitrate, 2.9×10^{-3} mole, gave 4.5×10^{-4} mole of sodium hydroxide required and 1.17×10^{-4} mole of silver bromide formed. This was similar to the chloride.

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The Reaction of Ketene Divinylacetal with Various Nitro Compounds[1,2]

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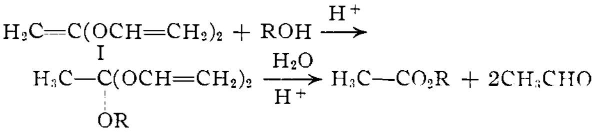
The preparation and reactions of ketene divinylacetal (I) have recently been reported by McElvain.[3] Compound I reacted with ethanol and 2-chloroethanol in the presence of catalytic amounts of acid to give the corresponding divinyl orthoacetates and with hydrogen chloride to form 1,1-divinyloxy-1-chloroethane.

This investigation consists of a study of addition reactions of nitro alcohols and nitro paraffins with ketene divinylacetal. 2-Nitroethanol, 2-nitro-1-butanol and 3-nitro-2-butanol reacted readily with I to form the corresponding divinyl nitroalkylorthoacetates (II, III and IV). These orthoacetates were high boiling liquids whose structures were established by elementary analysis and by hydrolysis to the corresponding nitroalkyl acetates.



$$\underset{\text{I}}{H_2C{=}C(OCH{=}CH_2)_2} + ROH \xrightarrow{H^+} \underset{\text{OR}}{H_3C{-}C(OCH{=}CH_2)_2} \xrightarrow[H^+]{H_2O} H_3C{-}CO_2R + 2CH_3CHO$$

R = $-(CH_2)_2NO_2$ (II)
R = $-CH_2CH(NO_2)CH_2CH_3$ (III)
R = $-CH(CH_3)CH(NO_2)CH_3$ (IV)

The orthoacetates (II and III) were readily polymerized, by heating alone or in the presence of benzoyl peroxide, to dark viscous liquids from which solid polymers were obtained by dissolution in acetone and precipitation into cold water. The elemental analyses of these polymers did not agree with any simple structure.

In contrast to compounds II and III, divinyl 3-nitro-2-butyl orthoacetate (IV) did not polymerize.

It was anticipated that nitro paraffins would be acidic enough to add to ketene divinylacetal in a manner similar to hydrogen chloride.[3] Nitromethane and 1,1-dinitroethane failed to react under acidic or basic conditions even though reflux temperatures were used. Only starting materials were recovered.

Experimental

Divinyl β-Nitroethyl Orthoacetate (II).—Six grams (0.053 mole) of ketene divinylacetal was placed in a 50-ml. distilling flask, immersed in an ice-bath and acidified with 2 drops of a solution of hydrochloric acid in nitroethanol (0.1 g. of concd. hydrochloric acid per ml. of nitroethanol). Then 4.8 g. (0.053 mole) of nitroethanol was added dropwise with stirring. The reaction was continued for 30 minutes and then the mixture was distilled under reduced pressure. A fraction of divinyl nitroethyl orthoacetate amounting to 5.6 g. (52%) was collected, b.p. 80–85° at 2 mm., $n^{25}D$ 1.4492.

Anal. Calcd. for $C_8H_{13}NO_5$: C, 47.29; H, 6.40; N, 6.89. Found: C, 47.31; H, 6.40; N, 7.10.

Divinyl 2-Nitro-1-butyl Orthoacetate (III).—The same procedure was used for the preparation of this compound as

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[1] Taken in part from the M.S. thesis of William H. Gardner, Purdue University, June, 1952.

[2] Financial support of this research was in part supplied by the United States Office of Naval Research.

[3] S. M. McElvain and A. N. Bolstad, THIS JOURNAL, **73**, 1988 (1951).

n the preparation of II. Six grams (0.053 mole) of ketene divinylacetal and 6.35 g. (0.053 mole) of 2-nitro-1-butanol were used. Upon fractional distillation, 5.2 g. (42.5%) of the orthoester III was collected, b.p. 90–93° at 2 mm., $n^{25}D$ 1.4480.

Anal. Calcd. for $C_{10}H_{17}NO_5$: C, 51.95; H, 7.41; N, 6.06. Found: C, 51.92; H, 7.70; N, 6.37.

Divinyl 3-Nitro-2-butyl Orthoacetate (IV).—The procedure for the preparation of II was followed. Five grams (0.044 mole) of ketene divinylacetal and 5.35 g. (0.044 mole) of 3-nitro-2-butanol reacted to yield 6.58 g. (63%) of divinyl 2-nitro-1-butyl orthoacetate, b.p. 85–86° at 2 mm., $n^{26}D$ 1.4512.

Anal. Calcd. for $C_{10}H_{17}NO_5$: C, 51.95; H, 7.41; N, 6.06. Found: C, 51.70; H, 7.55; N, 6.35.

Hydrolysis of the Orthoesters II, III and IV.—Each of these orthoesters was hydrolyzed by treatment of 1–2-g. samples of the orthoester with 3 drops of a 1% aqueous solution of sulfuric acid. The evolved acetaldehyde was collected and identified as its 2,4-dinitrophenylhydrazone and the corresponding nitroalkyl esters identified by physical properties previously reported in the literature.

Polymerization Studies.—Approximately 1-g. samples of divinyl β-nitroethyl orthoacetate (II), divinyl 2-nitro-1-butyl orthoacetate (III) and divinyl 3-nitro-2-butyl orthoacetate (IV) were placed in screw cap vials and a small amount of benzoyl peroxide was added to each. The vials were then immersed in an oil-bath maintained at 70°.

After 2 days, compound II had turned dark brown and viscous. The sirupy liquid was dissolved in 5 ml. of acetone and poured with stirring into 20 ml. of cold water. A finely divided brown precipitate was collected and dried. It was purified twice by dissolving it in acetone and precipitating into water. The polymer had no definite softening point but began to darken at about 100°.

At the end of 8 days, compound III had become dark and viscous. The solid was collected and purified in the same manner as described above. The dark brown polymer softened and darkened when heated above 115°.

Compound IV did not polymerize even after a heating period of ten days.

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Spectral Properties of Fluorine-containing Conjugated Esters[1]

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In a previous paper,[3] infrared absorption spectral data were presented for three types of fluorine-containing esters. The effect of the location of the fluorine atoms on the ester carbonyl frequency was noted and wave lengths were assigned for the C═O stretching vibrations. In particular, the spectrum of ethyl butyrate was compared with those of ethyl perfluorobutyrate, trifluoroethyl butyrate and trifluoroethyl perfluorobutyrate.

It was of interest, therefore, to introduce a vinyl group into the acid portion of each of these esters and to observe the effect of the resultant conjugation on the ester carbonyl frequency. In Table I the carbonyl stretching vibration for each of the conjugated esters is compared with that of the corresponding ethyl butyrate of which it is a vinylog.[4] The accuracy is considered to be ±0.02 μ.

Table I

Compound	C═O stretching vibration wave length, μ	Compound	C═O stretching vibration wave length, μ
$C_3H_7CO_2C_2H_5$	5.75	$C_3H_7CH{=}CH{-}CO_2C_2H_5$	5.81
$C_3H_7CO_2CH_2CF_3$	5.66	$C_3H_7CH{=}CH{-}CO_2CH_2CF_3$	5.74
$C_3F_7CO_2C_2H_5$	5.60	$C_3F_7CH{=}CH{-}CO_2C_2H_5$	5.75
$C_3F_7CO_2CH_2CF_3$	5.55	$C_3F_7CH{=}CH{-}CO_2CH_2CF_3$	5.67

Rasmussen and Brattain[5] have noted that conjugation of the ester C═O with C═C shifted the carbonyl band to longer wave lengths.

Ethyl butyrate and its vinylog, ethyl 2-hexenoate, illustrate this shift of the C═O band (5.75 μ to 5.81 μ). A similar shift of 0.08 μ is observed for the trifluoroethyl butyrate–trifluoroethyl 2-hexenoate pair. In this case, the inductive effect of the trifluoromethyl group is independent of the opposing conjugative effect. Thus, the fluorine atoms exert about the same influence on the C═O frequency that they would were conjugation not present. In earlier papers[3,6] the role of the inductive effect of the perfluoroalkyl group in shifting the C═O band to shorter wave lengths was discussed.

In ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate, $C_3F_7CH{=}CH{-}CO_2C_2H_5$, however, the inductive effect of the heptafluoropropyl group, transmitted through the vinyl linkage, is strongly opposed by resonance-stabilized conjugation.

There is sufficient evidence to substantiate this weakening of the inductive effect. Walborsky and Schwarz[7] determined the dissociation constant of 4,4,4-trifluorocrotonic acid as 7.1×10^{-4} in contrast with 5.8×10^{-1} for trifluoroacetic acid.[8] Analogous results have been reported for $C_3F_7CH{=}CH{-}CO_2H$[9] and $C_3F_7CO_2H$.[8] It has also been demonstrated[7] for ethyl trifluorocrotonate, that resonance of the carbethoxy group with the double bond, rather than the inductive effect, plays the dominant role in directing the addition of various reagents.

The observed C═O stretching frequency of $C_3F_7CH{=}CH{-}CO_2C_2H_5$ substantiates these results. While a shift of 0.15 μ to shorter wave lengths resulted from replacement of the hydrogens by fluorine in the acid portion of ethyl butyrate, a markedly smaller shift of only 0.06 μ is observed in the corresponding conjugated esters. A similar effect was noted by Rasmussen and Brattain in esters of nitrobenzoic acids.[5]

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[1] Opinions expressed are those of the author and do not necessarily express the official opinions of the U. S. Air Force or the Wright Air Development Center.

[2] Department of Chemistry, Ohio Wesleyan University, Delaware, Ohio.

[3] G. Rappaport, M. Hauptschein, J. F. O'Brien and R. Filler, This Journal, **75**, 2695 (1953).

[4] The infrared spectra referred to in this article have been deposited as Document number 4147 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35 mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

[5] R. S. Rasmussen and R. R. Brattain, This Journal, **71**, 1073 (1949).

[6] M. Hauptschein, C. S. Stokes and E. A. Nodiff, *ibid.*, **74**, 4005 (1952).

[7] H. M. Walborsky and M. Schwarz, *ibid.*, **75**, 3241 (1953).

[8] A. L. Henne and C. J. Fox, *ibid.*, **73**, 2323 (1950).

[9] E. T. McBee, O. R. Pierce and D. D. Smith, Abstracts, 124th National Meeting, American Chemical Society, Chicago, Ill., Sept., 1953, p. 24–0.