bonate support were suspended in 150 ml. of purified dioxane, and the material was reduced at a hydrogen pressure of 1800 p.s.i. at 150° for 4 hr. in a Parr high-pressure apparatus. The reaction mixture was filtered, the dioxane removed by distillation and the 4-ethoxycarbonylcyclohexanol was vacuum-distilled through a 50-cm. Vigreux column. Yield of 4-ethoxycarbonylcyclohexanol, 80%; b.p. 115–123° (4 mm.); n_D^{20} 1.4635.

4-Ethoxycarbonylcyclohexanone. 4-Ethoxycarbonylcyclohexanol was oxidized by the acid-dichromate method,[16] but because of possible hydrolysis of the ester grouping, the usual procedure was slightly modified in that the temperature was not allowed to rise above 35°. The crude 4-ethoxycarbonylcyclohexanone was vacuum-distilled through a 50-cm. Vigreux column and the product was collected. Yield of 4-ethoxycarbonylcyclohexanone, 65%; b.p. 112–118° (4 mm.); n_D^{25} 1.4594.

4-Ethoxycarbonyl-1,2-cyclohexanedione. The 4-ethoxycarbonylcyclohexanone was oxidized with alcoholic selenium dioxide to give the corresponding diketone. The method reported by Riley, Morley, and Friend[17] as modified by Hach, Banks, and Diehl[18] was employed. The reaction mixture was filtered and fractionated through a 50-cm. Vigreux column under reduced pressure. The dione is very unstable towards prolonged heating and the distillation should be completed as rapidly as possible. Yield of 4-ethoxycarbonyl-1,2-cyclohexanedione, 48%; b.p. 120–135° (2 mm.); n_D^{20} 1.4862.

4-Ethoxycarbonyl-1,2-cyclohexanedionedioxime. 4-Ethoxycarbonyl-1,2-cyclohexanedione was oximated by a method very similar to that of Bachmann and Boatner.[19] One-half mole of the dione, 2 moles of hydroxylammonium chloride, 4 moles of pyridine, and 600 ml. of absolute alcohol were refluxed for 35 min. on a steam bath. After most of the pyridine had evaporated, the oily mixture was poured into an equal volume of cold water to precipitate the crude 4-ethoxycarbonyl-1,2-cyclohexanedionedioxime. This material was dried and recrystallized twice from ethyl acetate. Yield of 4-ethoxycarbonyl-1,2-cyclohexanedionedioxime, 55%; m.p. 167°.

Analytical samples were obtained by dissolving 1 g. of the ester in 50 ml. of absolute ethanol and passing the solution through a column 10 cm. in length and 2.5 cm. in diameter packed with Woelm basic alumina. Ethanol was used as the eluant. The 4-ethoxycarbonyl-1,2-cyclohexanedionedioxime was precipitated from the ethanol by the addition of petroleum ether, filtered, and dried at 110° for 1 hr.

Anal. Calcd. for $C_9H_{14}N_2O_4$: N, 13.08%. Found: N, 12.97%; 13.15%.

4-Hydroxyaminocarbonyl-1,2-cyclohexanedionedioxime. 4-Hydroxyaminocarbonyl-1,2-cyclohexanedionedioxime can be prepared from 4-ethoxycarbonyl-1,2-cyclohexanedionedioxime by using the synthesis given for benzohydroxamic acid.[20] This compound gave a red precipitate with nickel while cupric acetate produced a greenish-blue color characteristic of hydroxamic acids. It was observed that this hydroxamic acid was hydrolyzed readily by aqueous acid solution, which is in agreement with the information reported in the review paper by Yale.[21] Yield of 4-hydroxyaminocarbonyl-1,2-cyclohexanedionedioxime 60%; m.p. 152°.

Anal. Calcd. for $C_7H_{11}N_3O_4$: N, 21.00%. Found: N, 21.10%; 20.81%.

4-Carboxy-1,2-cyclohexanedionedioxime. 4-Carboxy-1,2-cyclohexanedionedioxime was obtained by hydrolysis of 4-ethoxycarbonyl-1,2-cyclohexanedionedioxime. This was accomplished by heating on a steam bath for 1 hr. a mixture of 0.1 mole of the ester, 0.15 mole of potassium hydroxide, and 125 ml. of water. After cooling, the reaction mixture was acidified to *p*H 1–2. The precipitated acid was filtered and dried. More acid can be obtained by extraction of the hydrolysis mixture with diethyl ether. The acid was recrystallized by dissolving in a minimum amount of hot dioxane, adding petroleum ether to incipient cloudiness, cooling, and filtering. The acid had a purity of 95% based on micro Dumas nitrogen determinations and titration of the carboxy hydrogen.

Further purification can be obtained by dissolving approximately 2 g. of the acid in 50 ml. of dioxane and passing the solution, while hot, through a column 10 cm. in length and 2.5 cm. in diameter which was packed with a 1:1 mixture of acidic and basic Woelm alumina. This procedure was repeated twice and a very pure compound was obtained, as indicated by titration of the acid which gave a molecular weight of 186.16; theoretical is 186.17. Yield of 4-carboxy-1,2-cyclohexanedionedioxime, 50%; m.p. 218–220° with decomposition.

Anal. Calcd. for $C_7H_{10}N_2O_4$: N, 15.05%. Found: N, 15.08%; 15.04%.

pK Determinations. The molar dissociation constants for 4-carboxy-1,2-cyclohexanedionedioxime were determined by the following methods. The pK_1' for the carboxy hydrogen was determined by direct titration with 0.1*N* potassium hydroxide after having added a known excess of standardized 0.1*N* hydrochloric acid. A value of 4.75 ($\mu = 0.100$) was found. Conversion to the thermodynamic constant, pK_1, by application of the Debye and Hückel theory, gave a value of 4.85.

The method of Banks and Carlson[22] was used to determine the *p*K values of the oxime hydrogens. The average value found for four determinations of pK_2' was 10.44 ($\mu = 0.01$) and for two determinations of pK_3' was 12.31 ($\mu = 0.06$). Conversion to the thermodynamic constants gave 10.45 for pK_2 and 12.37 for pK_3.

Due to the hydrolysis of 4-hydroxyaminocarbonyl-1,2-cyclohexanedionedioxime the *p*K values were not determined.

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Reactivity Ratios of Trifluoromethyl-substituted Styrenes with Methyl Methacrylate and Styrene

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To find the effect of substitution of the trifluoromethyl group on the polymerization reactivity of styrene, the reactivity ratios of 3-

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TABLE I

REACTIVITY RATIO DETERMINATIONS

M_1	r_1	M_2	r_2
Styrene	.70±.05	3-Trifluoromethylstyrene	1.05±.05
Methyl methacrylate	.60±.10	3-Trifluoromethylstyrene	0.98±.15
Styrene	.45±.05	2,5-bis(Trifluoromethyl)styrene	1.15±.08
Methyl methacrylate	.57±.07	2,5-bis(Trifluoromethyl)styrene)	1.35±.05

trifluoromethylstyrene and 2,5-bis(trifluoromethyl)styrene with methyl methacrylate and styrene were determined by the method of Mayo and Lewis.[2] Polymerizations were run in bulk and the composition of the resultant polymers was determined by fluorine analysis. The error in the "r" values was estimated by assuming that the maximum error in elemental analysis (about ±0.25%) is the primary limiting factor.[3] The results are summarized in Table I.

The "r" values of these substituted styrenes are similar to those for halogen-substituted styrenes. Since the reactivity ratio is a measure of the tendency of one monomer to add to itself or to the comonomer, the results show that the substituted styrenes add to their own radical slightly faster than they add to the comonomer radical and that substitution of a second trifluoromethyl group increases this tendency.

Using the Price-Alfrey scheme with revised *Q* and *e* styrene and methyl methacrylate, the reactivity of 3-trifluoromethylstyrene, *Q*, and the polarity, *e*, were calculated to be 0.92 and −0.28 respectively. Values of $Q = 1.14$ and $e = -.04$ were calculated for 2,5-bis(trifluoromethyl)styrene.

TABLE II

REACTIVITY RATIO DETERMINATION WITH METHYL METHACRYLATE

Mole fraction[a]	$\frac{M_1}{M_2}$	Conversion, %	Analysis, %F	Mole fraction[b]	$\frac{M_2}{M_1}$
		3-Trifluoromethylstyrene			
0.100	9.03	6.3	7.62	0.148	0.174
0.252	2.97	6.0	14.24	0.305	0.439
0.400	1.50	4.5	19.54	0.455	0.837
0.498	1.01	5.2	22.52	0.552	1.234
0.600	0.67	6.0	22.50	0.660	1.943
		2,5-Bis(trifluoromethyl)styrene			
0.249	3.01	2.6	26.59	0.347	0.531
0.400	1.50	8.6	34.18	0.517	1.07
0.500	1.00	9.5	37.98	0.625	1.66
0.599	0.67	9.3	39.88	0.686	2.19
0.769	0.30	9.8	43.68	0.827	4.79

[a] Fluorine-containing styrene in charge. [b] Fluorine-containing styrene in polymer.

TABLE III

REACTIVITY RATIO DETERMINATION WITH STYRENE

Mole Fraction[a]	$\frac{M_1}{M_2}$	Conversion, %	Analysis, %F	Mole Fraction[b]	$\frac{M_2}{M_1}$
		3-Trifluoromethylstyrene			
0.103	8.75	7.4	6.62	0.131	0.151
0.253	2.95	6.3	14.24	0.313	0.457
0.402	1.49	7.0	19.21	0.455	0.836
0.500	1.00	6.4	22.19	0.551	1.227
0.599	0.67	8.6	24.67	0.639	1.767
		2,5-Bis(trifluoromethyl)styrene			
0.100	8.98	9.4	17.80	0.206	0.260
0.250	3.00	9.0	27.06	0.365	0.574
0.402	1.49	8.5	36.55	0.516	1.065
0.500	1.00	6.4	38.70	0.592	1.452

[a] Fluorine-containing styrene in charge. [b] Fluorine-containing styrene in polymer.

EXPERIMENTAL

Monomers. Commercial samples of styrene and methyl methacrylate were redistilled before use. The trifluoromethyl styrenes were prepared by Dr. E. T. McBee.[4]

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(2) F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.*, 66, 1594 (1944).

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Reactivity ratio determinations. Polymerization was carried out in bulk at 60° using 1.0% benzoyl peroxide initiator. The polymer was precipitated in methanol and unreacted monomer was extracted by low-boiling petroleum ether in a Soxhlet extractor for 6 hr. For further purification the polymer was twice reprecipitated from benzene or trifluoromethylbenzene. The conversion in these reactivity ratio studies were of the order of 5–10% and never more than 10%. The experimental data are summarized in Tables II and III.

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para-Nitrobenzyl Nitrite[1]

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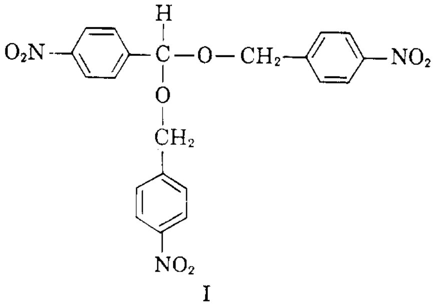
In the course of another study it became necessary to know something of the chemical properties of *p*-nitrobenzyl nitrite, a compound first prepared in 1955.[2]

p-Nitrobenzyl nitrite is a yellow liquid which has previously been reported[2] to decompose to a light yellow solid (uncharacterized) on standing overnight exposed to the atmosphere, in the dark, at room temperature. In the present study, the nitrite ester was protected from the atmosphere and allowed to decompose at room temperature in the dark; four days were required for complete solidification. During this time a colorless gas, which turned brown on contact with the air, and which attacked mercury, was evolved. The resulting light yellow solid was easily separated into two components: *p*-nitrobenzaldehyde (24% yield), and the acetal (I) of *p*-nitrobenzaldehyde with *p*-nitrobenzyl alcohol (72% yield). The colorless gas is presumably nitric oxide.



I

The formation of an acetal in the thermal decomposition of a nitrite ester is, to our knowledge, unprecedented. Another interesting feature is the relatively great instability of *p*-nitrobenzyl nitrite. While it is not difficult to imagine why *p*-nitrobenzaldehyde should go over to the acetal rather readily, it is less than obvious why *p*-nitrobenzyl nitrite is so unstable.

EXPERIMENTAL[3]

Decomposition of p-nitrobenzyl nitrite. p-Nitrobenzyl nitrite was prepared by the previously reported method[2] except that purification was accomplished by molecular distillation at *ca.* 10^{-3} mm. and room temperature; the distillate was kept at Dry Ice temperature as it was being collected. A 6.4-g. (0.035 mole) sample, n_{D}^{20} 1.5498; m.p. 12.5°, was protected from the atmosphere by a mercury valve and allowed to stand in the dark at room temperature. Sometime during the first 12 hr. the evolution of a colorless gas, which attacks mercury and which turns brown on contact with air, commenced. After 4 days all the liquid had disappeared and in its place a pale yellow solid, 5.2 g., m.p. 105–155° remained.

Digestion of this solid with refluxing acetone gave, upon cooling, the acetal (I), 3.9 g. (.0088 mole), m.p. 209–210° (72% yield). Evaporation of the acetone left 1.3 g. (0.009 mole, 24% yield) of *p*-nitrobenzaldehyde, m.p. 102–104°; recrystallization gave m.p. 105–106°, mixed m.p. with an authentic sample of m.p. 105–106°, was undepressed.

The dinitrophenylhydrazone prepared from the aldehyde had m.p. 318° (dec.); a mixed m.p. determination with the dinitrophenylhydrazone of authentic *p*-nitrobenzaldehyde, m.p. 318° (dec.), showed no depression.

Characterization of acetal (I). This chalk white solid, m.p. 209–210°, was insoluble in water, ethyl ether, and benzene and was slightly soluble in acetone, dioxane, and ethyl acetate. Recrystallization from acetone raised the m.p. of I to 210–211°. I does not react with aqueous potassium permanganate or dinitrophenylhydrazine reagent. It dissolves in cold concentrated sulfuric acid to give a colorless solution which, when poured on to ice gave straw yellow crystals, m.p. 100–102°. Recrystallization from water raised the m.p. to 105–106°; a mixed m.p. with authentic *p*-nitrobenzaldehyde, m.p. 105–106°, was undepressed. The dinitrophenylhydrazone had m.p. 318° (dec.), and a mixed m.p. with authentic dinitrophenyl hydrazone m.p. 318°, was undepressed.

Hydrolysis of 0.3 g. of the acetal (I) was also accomplished by heating under reflux for 4 hr. in 35 ml. of 43% aqueous dioxane containing 5 drops of concentrated hydrochloric acid. The resulting solution was cooled to room temperature and treated with benzoyl chloride and 10% aqueous sodium hydroxide; this gave *p*-nitrobenzyl benzoate m.p. 89–92°. Recrystallization from ethanol raised the m.p. to 92–93°. A mixed m.p. with an authentic sample of *p*-nitrobenzyl benzoate (m.p. 91–93°) gave m.p. 91–93°.

Anal. Calcd. for $C_{21}H_{17}N_3O_8$: C, 57.6; H, 3.90; N, 9.56. Found: C, 57.6; H, 3.77; N, 9.76.

Synthesis of the acetal of p-nitrobenzaldehyde and p-nitrobenzyl alcohol (I). *p*-Nitrobenzyl alcohol, 1.0 g. (0.0065 mole), and *p*-nitrobenzaldehyde, 0.5 g. (0.0033 mole), were dissolved in 50 ml. of dry benzene. One drop of 85% phosphoric acid was added and the benzene-water azeotrope was slowly distilled out; from time to time dry benzene was added to maintain the volume between 15 and 50 ml. The distillation was conducted for 16 hr. during which time 85 ml. of benzene distilled.

The precipitate which formed, even in the hot solution, was isolated by cooling the mixture to room temperature and filtering; 1.14 g. (80% yield), m.p. 204–210°. Recrystal-

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[1] (1) This work was supported by a grant from the Explosives Department of E. I. du Pont de Nemours and Co., Inc.

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[3] (3) Microanalyses by Dr. C. S. Yeh and Mrs. S. Margerum of this department.