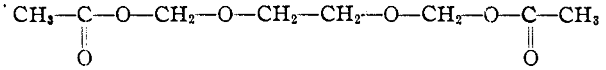
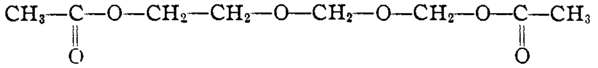
40° higher than the boiling point of 2,3-butanediol diacetate. This difference is in range that would be predicted for the —O—CH_2— grouping. Finally the work of Hudson and co-workers provides additional confirmation of these structures.

Attention is called to the fact that some of the above reactions of formals with acid anhydrides were accompanied by side reactions. This is evident from the examination of the yields of the expected products. Painstaking rectification of the by-products from the 1,3-dioxolane-acetic anhydride reaction led to the isolation of 1,2-ethanediol diacetate and a compound which is believed to be 2,5-dioxa-1,5-hexanediol diacetate



$$CH_3-\underset{\underset{O}{\|}}{C}-O-CH_2-O-CH_2-CH_2-O-CH_2-O-\underset{\underset{O}{\|}}{C}-CH_3$$

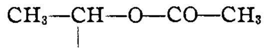
This structure is supported by elementary analysis, saponification equivalent and molecular refraction, although these same data would not exclude 2,4-dioxa-1,6-hexanediol diacetate



$$CH_3-\underset{\underset{O}{\|}}{C}-O-CH_2-CH_2-O-CH_2-O-CH_2-O-\underset{\underset{O}{\|}}{C}-CH_3$$

which could form under the conditions of the experiment. The product at hand may also be a mixture of these two compounds, the former probably being predominant in the mixture.

Each of the reactions of cyclic acetals other than formals with acetic anhydride gave acetic acid, the diacetate of the glycol for which the acetal was derived and a tar. These products may result from the decomposition of intermediates similar in structure to the compounds derived from the cyclic formals. For example 2,2,4,5-tetramethyl-1,3-dioxolane may first react with acetic anhydride to give 2,4-dimethyl-3-oxa-1,5-hexanediol diacetate



$$\begin{array}{l} CH_3-CH-O-CO-CH_3 \\ \qquad\ | \\ CH_3-CH-O-C(CH_3)_2-O-CO-CH_3 \end{array}$$

which reacts further with acetic anhydride to give 2,3-butanediol diacetate and isopropylidene diacetate. The latter decomposes to acetic acid and 1-propene-2-ol acetate which polymerizes to a tar in the presence of sulfuric acid at the elevated temperature of the experiment.

Acknowledgment.—The author is indebted to Professor C. D. Hurd for naming the new compounds which are described in this paper.

Summary

The reactions of acid anhydrides with some cyclic acetals derived from dihydric alcohols have been investigated.

4,5-Dimethyl-1,3-dioxolane (2,3-butanediol formal) reacted almost quantitatively with sulfuric acid acetic anhydride to give 3-methyl-2-oxa-1,4-butanediol diacetate

$$CH_3-CO-O-CH_2-O-CH(CH_3)-CH(CH_3)-O-CO-CH_3$$

and with sulfuric acid butyric anhydride to give the corresponding dibutyrate.

Each of the other cyclic formals that was studied reacted with sulfuric acid acetic anhydride to give as a main product a similar diacetate. 1,3-Dioxolane gave in addition in small yields 1,2-ethanediol diacetate and a compound which is likely 2,5-dioxa-1,6-hexanediol diacetate and 1,3-dioxane gave in addition in small yields 1,3-propanediol diacetate and a compound which is believed to be 2,6-dioxa-1,7-heptanediol diacetate.

4,5-Dimethyl-1,3-dioxolane has been converted to 2,3-butanediol diacetate and formaldehyde.

The cyclic acetals other than formals failed to react with 1% sulfuric acid acetic anhydride at 100° in two hours. Prolonged refluxing of each of these mixtures yielded acetic acid, the diacetate of the glycol from which the acetal was derived and a tar.

Terre Haute, Indiana Received August 22, 1945

[Contribution from the Noyes Chemical Laboratory, University of Illinois]

The Preparation and Polymerization of Some Substituted Styrenes[1,2]

By C. S. Marvel, C. G. Overberger, R. E. Allen and J. H. Saunders

In order to investigate the effects of different groups on the polymerization and copolymerization of styrene derivatives, a study of a wide variety of styrenes has been in progress in this Laboratory. This paper reports a method of synthesis for the new *m*-trifluoromethylstyrene and gives some details on new procedures for the preparation of *m*-methylstyrene[3] and *m*-nitrostyrene[4] and abnormalities of *p*-N,N-dimethylaminostyrene.[5] In addition a brief summary of the properties of the polymers of these styrenes is given. The copolymerization studies will be reported later. It should be noted that *m*-nitrostyrene does not polymerize or copolymerize under

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[1] This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

[2] This is the twentieth communication on vinyl polymers. For the nineteenth, see This Journal, **67**, 2250 (1945).

[3] (a) Müller, *Ber.*, **20**, 1215 (1887); (b) Titley, *J. Chem. Soc.*, 517 (1926); (c) Shorygin and Shorygina, *J. Gen. Chem.*, *U. S. S. R.*, **5**, 555 (1935).

[4] Prausnitz, *Ber.*, **17**, 596 (1884).

[5] v. Braun and Blessing, *ibid.*, **56**, 2154, 2161 (1923).

the conditions of peroxide catalysis which we have used.

m-Trifluoromethylstyrene

m-Bromotrifluoromethylbenzene was prepared satisfactorily both by the procedure of Finger and Kalinowski[6] and that of Simons and Ramler.[7] The Grignard reagent from this halide was condensed with acetaldehyde to give *m*-trifluoromethylphenylmethylcarbinol which was readily dehydrated to the desired styrene.

***m*-Trifluoromethylphenylmethylcarbinol.**—Into a 5-liter, three-necked, round-bottomed flask equipped with a stirrer, condenser, and dropping funnel were placed 76.3 g. (3.14 gram-atoms) of magnesium turnings and 50 cc. of dry ether. A solution of 706.5 (3.14 moles) of *m*-trifluoromethylbromobenzene in 2000 cc. of dry ether was added slowly with stirring over a period of two hours. To this solution was added, with stirring, a solution of 160 g. (3.63 moles) of freshly-distilled acetaldehyde in 1800 cc. of dry ether. The reaction mixture was allowed to reflux an additional four hours. The complex was decomposed with a saturated solution of ammonium chloride. The ether layer was removed and the aqueous layer was extracted with 500 cc. of ether. The combined ether solutions were washed with water, with 500 cc. of a 5% solution of sodium bicarbonate, again with water, and dried over anhydrous sodium sulfate. After removing the solvent, the residue was distilled through a helices-packed column. The product boiled at 100–102° (17 mm.), n^{20}D 1.4585, d^4_{20} 1.2485. The yield was 495 g. (2.6 moles) or 83% of the theoretical amount.

Anal.[8] Calcd. for $C_9H_9OF_3$: C, 56.84; H, 4.77. Found: C, 57.02; H, 4.94.

***m*-Trifluoromethylstyrene.**—The procedure was adapted from that of Marvel and Brown[9] for related compounds. Into a 2-liter, round-bottomed flask equipped with a condenser were placed 495 g. (2.6 moles) of *m*-trifluoromethylphenylmethylcarbinol dissolved in 1300 cc. of dry benzene and 185 g. of phosphorus pentoxide. This reaction mixture was refluxed gently for four hours. The benzene solution was decanted from the phosphoric acid and the solvent was removed. The residue was distilled through a helices-packed column. The product boiled at 55° (17 mm.), n^{20}D 1.4655, d^4_{20} 1.1587. The yield was 240.5 g. (1.40 moles) or 53.7% of the theoretical amount.

Anal. Calcd. for $C_9H_7F_3$: C, 62.79; H, 4.10. Found: C, 62.81; H, 4.14.

m-Methylstyrene

m-Methylstyrene has been prepared by the dehydration of β-(*m*-methylphenyl)-ethyl alcohol,[3c] by the decomposition of trimethyl-β-(*m*-methylphenyl)-ethylammonium hydroxide[3b] and by the decomposition of β-bromo-β-phenylpropionic acid.[3a] We have now prepared it by dehydration of *m*-tolylmethylcarbinol which was obtained by the action of *m*-tolylmagnesium bromide on acetaldehyde.

***m*-Tolylmethylcarbinol.**—The Grignard reagent from 598 g. (3.5 moles) of *m*-bromotoluene was treated with acetaldehyde to give 338 g. (2.48 moles) (71%) of *m*-tolylmethylcarbinol boiling at 103–105° (6 mm.), n^{20}D 1.5240. v. Auwers[10] has prepared this compound from *m*-methylbenzaldehyde, b. p. 108–109.4° (12 mm.), n^{20}D 1.5243.

***m*-Methylstyrene.**—Dehydration of 338 g. (2.48 moles) of the above carbinol by the procedure of Brooks[11] for related compounds gave 147 g. (1.25 moles, 50%) of *m*-methylstyrene, b. p. 50–51° (3 mm.), n^{20}D 1.5410 which gave a dibromide melting at 45° as reported by Titley.[3b] Shorygin and Shorygina[3c] reported n^{24}D 1.5400 for *m*-methylstyrene.

m-Nitrostyrene

Prausnitz[4] added hydrogen bromide to *m*-nitrocinnamic acid and then decomposed the product with sodium carbonate to make *m*-nitrostyrene. We have reduced *m*-nitroacetophenone with aluminum isopropoxide[12] and dehydrated the carbinol to give *m*-nitrostyrene.

Into a 1-liter round-bottomed flask were placed 57 g. (0.34 mole) of *m*-nitrophenylmethylcarbinol, 500 cc. of dry benzene, 5.0 g. of phosphorus pentoxide, and a trace of *p*-*t*-butylcatechol. A reflux condenser was attached to the flask, and the mixture refluxed by means of a steam cone for five and one-half hours.

At the end of this time, the benzene layer was decanted from the acid layer and the benzene removed by distillation. The residue was submitted to a steam distillation in order to separate the more volatile *m*-nitrostyrene from the carbinol. The distillate was extracted with two 100-cc. portions of carbon tetrachloride.

The non-volatile residue from the steam distillation was extracted with two 100-cc. portions of benzene; the extracts were combined and dried over 10 g. of anhydrous sodium sulfate. The drying agent was removed and the benzene solution diluted to 500 cc. with dry benzene. The benzene solution again was treated with phosphorus pentoxide, and the carbinol and styrene were separated as before. This same procedure was repeated again to ensure complete utilization of all the carbinol which was employed in the reaction.

The total carbon tetrachloride extracts from the distillates of the three steam distillations were dried over 20 g. of anhydrous sodium sulfate. The solvent and drying agent were removed, and a trace of *p*-*t*-butylcatechol was added. The residue was distilled through a 125-cc. modified Claisen flask under reduced pressure.

The following fractions were obtained: 2.8 g., b. p. 93–95° (3 mm.), n^{20}D 1.5808; 2.8 g., b. p. 95–96° (3 mm.), n^{20}D 1.5819; 12.7 g., b. p. 96–100° (3 mm.), n^{20}D 1.5818; 0.4 g., b. p. 102° (3 mm.), n^{20}D 1.5794. The third fraction was submitted for analysis and proved to be pure *m*-nitrostyrene.

Anal. Calcd. for $C_8H_7O_2N$: C, 64.42; H, 4.73. Found: C, 64.57; H, 4.72.

This nitrostyrene did not polymerize when treated in bulk with benzoyl peroxide or ultraviolet light and it did not polymerize alone or with butadiene when an emulsion of water and soap was treated with potassium persulfate.

p-N,N-Dimethylaminostyrene

v. Braun and Blessing[5] obtained this compound by the decomposition of trimethyl-β-(*p*-N,N-dimethylaminophenyl) ethyl ammonium hydroxide. We have prepared it by modifying the procedure of Sachs and Sachs[13] for making *p*-N,N-dimethylaminophenylmethylcarbinol which dehydrated to the styrene during its isolation from the reaction mixture. The melting point of our picrate of *p*-N,N-dimethylaminostyrene does not agree with that of v. Braun and Blessing.[5]

Into a 1-liter, three-necked, round-bottomed flask equipped with dropping funnel, condenser, and stirrer, was placed 5 g. of magnesium turnings (0.206 gram-atom) covered with 15 cc. of dry ether. To this was added 30 g. (0.21 mole) of methyl iodide dissolved in 250 cc. of dry ether. The mixture was stirred for an additional half-hour after complete addition of the methyl iodide solution. To this with stirring was added 25 g. (0.17 mole) of *p*-dimethylaminobenzaldehyde dissolved in 400 cc. of ether. The addition took from one to two hours. The Grignard complex was decomposed with a saturated ammonium chloride solution to which 5 cc. of concentrated hydrochloric acid had been added. The ether solution was separated, and the aqueous layer (basic) was extracted

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[6] Finger and Kalinowski, *Trans. Illinois State Acad. Sci.*, **37**, 66 (1944).

[7] Simons and Ramler, THIS JOURNAL, **65**, 391 (1943).

[8] Microanalyses by Mr. H. S. Clark, Illinois State Geological Survey.

[9] Marvel and Brown, THIS JOURNAL, **59**, 1177 (1937).

[10] v. Auwers, *Ann.*, **408**, 242 (1915).

[11] Brooks, THIS JOURNAL, **66**, 1295 (1944).

[12] Lund, *Ber.*, **70**, 1520 (1937).

[13] Sachs and Sachs, *ibid.*, **38**, 512 (1905).

with an additional 150 cc. of ether. The combined ether solutions were dried with magnesium sulfate. The drying agent and ether were removed, and the residue was distilled from a 50-cc. Claisen flask. The *p*-dimethylaminostyrene boiled at 85–90° (2.5 mm.). If any dehydration occurred on distillation the water was separated, the product redissolved in ether and dried again. Redistillation in a three-plate, helices-packed column gave a boiling point of 90–91° (2.5–3 mm.); $n^{20}D$ 1.6010. The yield was 11 g. or 45% of the theoretical amount. Several experiments produced lower yields with a large amount of polymeric residue. A high-boiling polymeric residue could not be distilled.

Anal.[14] Calcd. for $C_{10}H_{13}N$: C, 81.58; H, 8.89. Found: C, 81.44; H, 8.91.

A picrate was obtained as a yellow powder from 95% ethanol, m. p. 93–94°.

If the product from the decomposition of the Grignard complex was not distilled, a small yield of white crystals was obtained, which, when recrystallized from petroleum ether, melted at 58.5–59°. Sachs and Sachs[12] report 60° for *p*-N,N-dimethylaminophenylmethylcarbinol.

Anal. Calcd. for $C_{10}H_5ON$: N, 8.39. Found: N, 8.37.

Polymerization of *m*-Trifluoromethylstyrene and *m*-Methylstyrene.—In a Pyrex test-tube was placed 1 g. of the monomer. The test-tube was suspended under an ultraviolet lamp and left there until a hard polymer had been formed (twenty-four hours). The polymer was dissolved in 50 cc. of benzene and precipitated by slowly dropping the solution into 300 cc. of methanol with vigorous mechanical stirring. This process was repeated and the powder obtained was dried for one week in a vacuum desiccator.

Polymerization of *p*-N,N-Dimethylaminostyrene. (A) Bulk.—About 1 g. of *p*-N,N-dimethylaminostyrene was heated for twenty-four hours at 120° in a small test-tube. At the end of this period a hard resin, completely soluble in benzene, had formed.

(B) Solution.—In a 25-cc. Erlenmeyer flask was placed 0.8 g. of *p*-N,N-dimethylaminostyrene, a small amount of benzoyl peroxide, and 15 cc. of purified dioxane. This was gently refluxed for twenty-four hours. The cooled solution was slowly dropped into 200 cc. of methyl alcohol with vigorous stirring. No powder or gum precipitated, and the solution was then evaporated to dryness. A heavy gum resulted, completely soluble in benzene. An attempt to precipitate this gum as a powder failed.

The following table summarizes the data on these polymers.

TABLE I

Polymer, -styrene			*m*-Trifluoromethyl	*m*-Methyl-	*p*,N,N-Dimethylamino- bulk
Approx. mol. wt.[a]			7346	33000	1620
Softening point, °C.			130–155	117–122	80–95
Solubility in benzene			+	+	+
Empirical formula			$C_9H_7F_3$	C_9H_{10}	$C_{10}H_{13}N$
Analyses, %	Calcd.	C	62.79	91.46	81.58
		H	4.10	8.54	8.89
		N	...	...	9.51
	Found	C	62.73	90.08	80.45
		H	4.25	8.26	8.09
		N	...	...	8.77

[a] These approximate molecular weights were determined by viscosity measurements with the use of an equation developed by Kemp and Peters for the determination of the molecular weight of polystyrene using the *K* value for styrene [Kemp and Peters, *Ind. Eng. Chem.*, **34**, 1097 (1942)].

Summary

1. The preparation of *m*-trifluoromethyl-styrene is described. New procedures for the preparation of *m*-methylstyrene, *m*-nitrostyrene and *p*-N,N-dimethylaminostyrene have been developed.

2. The polymers of these monomers, except *m*-nitrostyrene, have been prepared and characterized.

URBANA, ILLINOIS RECEIVED JANUARY 15, 1946

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[14] Microanalyses by Miss Theta Spoor, University of Illinois.

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

Studies in the Synthesis of the Antirachitic Vitamins. II. Δ^5-Androstenol-3 and its Partial Dehydrogenation with Benzoquinone[1,2]

BY NICHOLAS A. MILAS AND CHARLES R. MILONE[3]

The simplest sterol which would have the same nuclear structure as that found in the antirachitic provitamins is $\Delta^{5,7}$-androstadiene-3-ol. This could be prepared from Δ^5-androstenol-3, either by the method of Windaus, Lettré and Schenck[4] or that of Milas and Heggie.[5] When the latter method was used, a product was obtained which contained 16% of $\Delta^{5,7}$-androstadiene-3-ol. Irradiation of this crude product under standard conditions produced a mixture which was biologically inactive at a level of 4000 U. S. P. XI units of vitamin D per gram.[6] $\Delta^{5,7}$-Androstadiene-3,17-diol,[7] another simple sterol containing the provitamin D nuclear structure, was found to form no antirachitic products upon irradiation.[6,8] Two explanations may be advanced for the failure of these simple substances to form antirachitically active products upon irradiation. Much longer time of irradiation than that used under standard conditions may be

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(1) Last paper, Milas and Alderson, Jr., THIS JOURNAL, **61**, 2534 (1939).

(2) The present paper was originally submitted on March 20, 1940.

(3) Abstracted from a portion of a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry, M. I. T., August, 1939. Present address: Goodyear Rubber Company.

(4) Windaus, Lettré and Schenck, *Ann.*, **520**, 98 (1935).

(5) Milas and Heggie, THIS JOURNAL, **60**, 984 (1938); Sah, *Rec. trav. chim.*, **59**, 454 (1940); *cf.* Criegee, *Ber.*, **69B**, 2758 (1935); Arnold and Collins, THIS JOURNAL, **61**, 1407 (1939).

(6) Reported to the authors by Professor Robert S. Harris.

(7) Butenandt, Hausemann, Dresler and Meinster, *Ber.*, **71B**, 1316 (1938).

(8) Dimroth and Paland, *ibid.*, **72B**, 187 (1939).