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Summary

A simple method for the quantitative recovery of the carbon dioxide produced by the oxidation of certain glycosides and polyhydroxy compounds through the use of lead tetraacetate is described. This reaction is very useful and is now being used in the degradation of radioactive glucose, prepared photosynthetically.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE PURDUE RESEARCH FOUNDATION, PURDUE UNIVERSITY]

Preparation and Polymerization of Trifluoromethyl- and Chloro-(trifluoromethyl)-substituted Styrenes

BY EARL T. MCBEE AND ROBERT A. SANFORD[1]

In a study of the properties of chloro-(trifluoromethyl)-benzene and bis-(trifluoromethyl)-benzene, a number of bromo derivatives of these substances have been prepared.[2] The substitution of the bromine atom in these compounds by a vinyl group was accomplished and the resulting products were polymerized.

Some trifluoromethyl-substituted styrenes have been reported previously.[3,4] The synthesis of the monomers comprised the dehydration of substituted α-methylbenzyl alcohols which were prepared by means of the Grignard reagent. The Grignard reaction was conducted with bromo, bromochloro and bromodichloro derivatives of (trifluoromethyl)-benzene and bis-(trifluoromethyl)-benzenes. In each instance in which an organometallic compound was formed, the magnesium reacted with the bromine substituent. No reaction between magnesium and chlorine or fluorine was observed.

A trifluoromethyl group ortho to the bromine atom may slightly retard the formation of the Grignard reagent. Otherwise, the trifluoromethyl group seemed to have little, if any, effect on the Grignard reaction. However, in no instance was a Grignard reagent formed from compounds in which a chlorine atom was ortho to the bromine. The compounds which failed to react with magnesium as well as those which did react are listed in Table I.

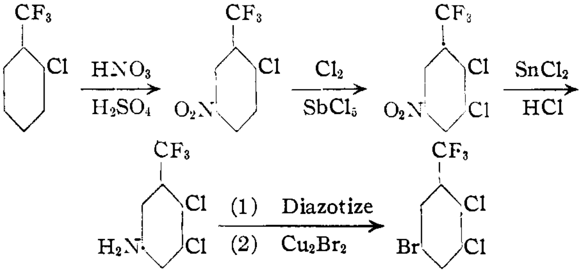
The Grignard reagents were condensed with acetaldehyde and the product hydrolyzed to the substituted α-methylbenzyl alcohols. These alcohols are listed in Table II. The dehydration of these alcohols was accomplished with a suspension of phosphorus(V) oxide in dry benzene at room temperature. The substituted styrene monomers were polymerized by an emulsion technique and the average molecular weights of the resulting polymers determined by the viscosity method. The monomers are listed in Table III.

TABLE I

REACTION OF SUBSTITUTED BROMOBENZENES WITH MAGNESIUM IN ETHER

(Trifluoromethyl)-benzene reacted	(Trifluoromethyl)-benzene failed to react
5-Bromo-2-chloro-	3-Bromo-4-chloro-
2-Bromo-5-chloro-	4-Bromo-3-chloro-
5-Bromo-2,3-dichloro-	5-Bromo-2,4-dichloro-
2-Bromo-1,4-bis-	5-Bromo-3,4-dichloro-
5-Bromo-1,3-bis-	5-Bromo-4-chloro-1,3-bis-
4-Bromo-1,2-bis-	2-Bromo-3,4-dichloro-1,5-bis-
2-Bromo-5-chloro-1,4-bis-	
5-Bromo-2-chloro-1,3-bis-	

Since the bromination of 2,3-dichloro-(trifluoromethyl)-benzene did not produce 5-bromo-2,3-dichloro-(trifluoromethyl)-benzene, this compound was prepared by



Acknowledgment.—The authors are indebted to the Ethyl Corporation and to the Westinghouse Electric Company for financial support which made this investigation possible.

Experimental

Preparation of Starting Materials

5-Bromo-2-chloro-(trifluoromethyl)-benzene, 3-bromo-4-chloro-(trifluoromethyl)-benzene, 2-bromo-5-chloro-(trifluoromethyl)-benzene, 4-bromo-3-chloro-(trifluoromethyl)-benzene, 5-bromo-2,4-dichloro-(trifluoromethyl)-benzene, 5-bromo-3,4-dichloro-(trifluoromethyl)-benzene, 2-bromo-1,4-bis-(trifluoromethyl)-benzene, 5-bromo-1,3-bis-(trifluoromethyl)-benzene, 4-bromo-1,2-bis-(trifluoromethyl)-benzene, 2-bromo-5-chloro-1,4-bis-(trifluoromethyl)-benzene, 5-bromo-2-chloro-1,3-bis-(trifluoromethyl)-benzene, 5-bromo-4-chloro-1,3-bis-(trifluoromethyl)-benzene and 2-bromo-3,4-dichloro-1,5-bis-(trifluoromethyl)-benzene were prepared by the bro-

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(1) Abstracted from the doctoral thesis of Robert A. Sanford.

(2) E. T. McBee, R. A. Sanford and P. J. Graham, THIS JOURNAL, **72**, 1651 (1950).

(3) M. W. Renoll, *ibid.*, **68**, 1159 (1946).

(4) G. B. Bachman and L. L. Lewis, *ibid.*, **69**, 2022 (1947).

TABLE II

SUBSTITUTED α-METHYLBENZYL ALCOHOLS

Compound	Yield, %	M. p., °C.	B. p., °C.	B. p., Mm.	n^{23}D	d^{23}_4	Fluorine, % Calcd.	Fluorine, % Found	Chlorine, % Calcd.	Chlorine, % Found
4-Cl-3-CF_3-C_8H_8O	71.5	-15^a	109.0	6	1.4853	1.3672	25.4	26.0	15.8	16.1
4-Cl-3-CF_3-α-CH_3-C_8H_7O	66.1	16.5–17.0	97.0	3	1.4834	1.3182	23.9	23.9	14.9	15.0
4-Cl-2-CF_3-C_8H_8O	78.5	-13^a	95.5	6	1.4829	1.3609	25.4	25.1	15.8	15.9
3,4-Cl_2-5-CF_3-C_8H_7O	77.0	50.0–51.0	110.5	3	....	....	22.0	21.2	27.4	27.3
2,5-$(CF_3)_2$-C_8H_8O	79.6	50.5–51.0	77.5	6	....	....	44.2	43.7	...	...
3,5-$(CF_3)_2$-C_8H_8O	73.0	69.0–69.5	83.0	6	....	....	44.2	44.3	...	...
3,4-$(CF_3)_2$-C_8H_8O	70.2	-15^a	98.5	6	1.4309	1.4209	44.2	43.8	...	...
4-Cl-2,5-$(CF_3)_2$-C_8H_7O	70.6	48.0–49.0	95.0	6	....	....	38.9	38.6	12.1	12.5
4-Cl-3,5-$(CF_3)_2$-C_8H_7O	66.0	71.0–72.0	105.0	6	....	....	38.9	38.3	12.1	11.9

[a] Sets to a glass.

TABLE III

SUBSTITUTED STYRENES

Compound	Yield, %	M. p., °C.	B. p., °C.	B. p., Mm.	n^{26}D	d^{t}_4	t, °C.	Fluorine, % Calcd.	Fluorine, % Found	Chlorine, % Calcd.	Chlorine, % Found	Polymer av. mol. wt.
4-Cl-3-CF_3-C_8H_6	77.0	−26.0 to −25.5	69	6	1.4980	1.3047	28	27.6	28.2	17.2	17.2	55,400
4-Cl-3-CF_3-α-CH_3-C_8H_5	82.4	−32.0 to −31.0	64	2.5	1.4944	1.2737	25	25.8	25.2	16.1	16.6	5,500
4-Cl-2-CF_3-C_8H_6	78.0	−15.2 to −15.0	56	6	1.4919	1.2967	27	27.6	27.9	17.2	17.4	18,500
3,4-Cl_2-5-CF_3-C_8H_5	74.0	19.5 to 20.0	75	3	1.5200	1.4369	27	23.6	23.4	29.5	29.3	28,100
2,5-$(CF_3)_2$-C_8H_6	81.9	−48.0 to −47.0	58	20	1.4237	1.3342	30	47.5	48.1	...	...	56,100
3,5-$(CF_3)_2$-C_8H_6	80.0	7.0 to 8.0	60	20	1.4220	1.3341	25	47.5	47.0	...	...	40,800
3,4-$(CF_3)_2$-C_8H_6	77.0	−31.0 to −30.5	78	20	1.4370	1.3705	23	47.5	47.1	...	...	29,600
4-Cl-2,5-$(CF_3)_2$-C_8H_5	67.0	6.0 to 6.5	78	20	1.4512	1.4441	27	41.5	41.8	12.9	13.2	20,400
4-Cl-3,5-$(CF_3)_2$-C_8H_5	73.0	17.0 to 17.5	68	6	1.4592	1.4689	27	41.5	41.3	12.9	12.8	22,700

mination of the corresponding chloro-(trifluoromethyl)-benzene, chloro-bis-(trifluoromethyl)-benzenes and bis-(trifluoromethyl)-benzenes following procedures described previously.[2]

Preparation of 5-Bromo-2,3-dichloro-(trifluoromethyl)-benzene

2-Chloro-5-nitro-(trifluoromethyl)-benzene.—A mixture of 542 g. of 2-chloro-(trifluoromethyl)-benzene and 750 ml. of sulfuric acid (96.7%) was treated with a solution composed of 450 ml. of nitric acid (69.5%) and an additional 450 ml. of sulfuric acid. The nitration reaction was performed at 15° and there resulted 630 g. (93.4%) of 2-chloro-5-nitro-(trifluoromethyl)-benzene,[5] b. p. 103–104° (10 mm.).

2,3-Dichloro-5-nitro-(trifluoromethyl)-benzene.—2-Chloro-5-nitro-(trifluoromethyl)-benzene (340 g.) was chlorinated in a 1-l. iron autoclave at 125° for a period of twenty-four hours. Chlorine (100 g.) was condensed in the autoclave and 50 g. of antimony(V) chloride was added as a halogen carrier. The reaction mixture was washed with sodium hydrogen sulfite, steam distilled and the organic distillate dried with anhydrous sodium sulfate. On rectification, there was obtained 95.0 g. of unreacted 2-chloro-5-nitro-(trifluoromethyl)-benzene and 106 g. (38.5%) of 2,3-dichloro-5-nitro-(trifluoromethyl)-benzene, b. p. 116° (10 mm.), m. p. 17–17.5°, d^{23}_4 1.6454, n^{25}D 1.5237. Considerable decomposition was observed in the reaction and 27 g. of higher boiling residue remained in the still pot.

Anal. Calcd. for $C_7H_2Cl_2F_3NO_2$: Cl, 27.3; mol. wt., 260. Found: Cl, 26.8; mol. wt., 258.

5-Amino-2,3-dichloro-(trifluoromethyl)-benzene.—The reduction of 2,3-dichloro-5-nitro-(trifluoromethyl)-benzene was accomplished with a yield of 80.2% following a procedure given in "Organic Syntheses."[6] From 166 g. of 2,3-dichloro-5-nitro-(trifluoromethyl)-benzene, 600 g. of hydrated stannous chloride and 800 ml. of concentrated hydrochloric acid, there resulted 12 g. of unreacted 2,3-dichloro-5-nitro-(trifluoromethyl)-benzene, and 116 g. of 5-amino-2,3-dichloro-(trifluoromethyl)-benzene, b. p. 132° (10 mm.), m. p. 55.5–56°.

Anal. Calcd. for $C_7H_4Cl_2F_3N$: Cl, 31.0. Found: Cl, 30.8.

5-Bromo-2,3-dichloro-(trifluoromethyl)-benzene.—5-Amino-2,3-dichloro-(trifluoromethyl)-benzene (116 g.) was diazotized[7] in a solution of 98 g. of concentrated sulfuric acid in one-half liter of water to which was added slowly 75 ml. of water containing 35 g. of sodium nitrite. The diazonium salt was treated with an excess of freshly prepared cuprous bromide solution. The product was steam distilled, separated from the aqueous layer, dried, and rectified under 20 mm. of pressure. The distillate was composed of 10.5 g. of a pre-run boiling between 80–110° and 52.0 g. (35.5%) of 5-bromo-2,3-dichloro-(trifluoromethyl)-benzene, b. p. 110–110.2° (20 mm.); m. p. 9.5–10°, n^{25}D 1.5259, d^{25}_4 1.8365.

Anal. Calcd. for $C_7H_2BrCl_2F_3$: F, 19.4; Cl, 24.2; Br, 27.2. Found: F, 19.2; Cl, 24.0; Br, 27.0.

To confirm the position of the halogens, a sample of the 5-bromo-2,3-dichloro-(trifluoromethyl)-benzene was hydrolyzed to the corresponding benzoic acid and decarboxylated with copper chromite. A small amount of an oil was isolated which melted at 23–24°. This corresponds to the previously reported value for 4-bromo-1,2-dichlorobenzene.[8]

Preparation of 4-Chloro-3-(trifluoromethyl)-styrene

4-Chloro-3-(trifluoromethyl)-α-methylbenzyl alcohol.—The Grignard reagent of 200 g. of 5-bromo-2-chloro-(trifluoromethyl)-benzene was prepared in the usual manner. The reagent dissolved in 500 ml. of ether reacted with 35.2 g. of acetaldehyde in 100 ml. of ether. The addition product was hydrolyzed with 75 ml. of saturated ammonium chloride solution and 127 g. of 4-chloro-3-(trifluoromethyl)-α-methylbenzyl alcohol, b. p. 109–109.5° (6 mm.), was obtained.

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(5) H. W. Daudt and H. E. Woodward (to du Pont), U. S. Patent 2,212,825; August 27, 1940.

(6) "Organic Syntheses," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 255.

(7) "Organic Syntheses," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 136.

(8) W. H. Hurtley, *J. Chem. Soc.*, **79**, 1297 (1901).

4-Chloro-3-(trifluoromethyl)-styrene.—A suspension of 8.5 g. of phosphorus(V) oxide in 150 ml. of dry benzene was added to 35.0 g. of 4-chloro-3-(trifluoromethyl)-α-methylbenzyl alcohol and 1 g. of hydroquinone. The mixture was shaken vigorously at about 25°. When there was no increase in temperature upon further shaking, usually after about fifteen minutes, the benzene layer was decanted from the partially hydrated phosphorus(V) oxide and rectified through a 2-foot column packed with glass helices. An additional gram of hydroquinone was added before rectification. The distillate contained 24.5 g. of 4-chloro-3-(trifluoromethyl)-styrene, b. p. 68–69° (6 mm.).

All of the styrenes listed in Table III were prepared by the same method.

Emulsion Polymerization of Trifluoromethyl- and Chloro-(trifluoromethyl)-substituted Styrenes.—Samples of the styrenes were polymerized under comparable conditions. The polymerizations were performed at 50° under atmospheric pressure in a 3-necked flask (300 ml.) fitted with an efficient stirrer and a thermometer. Five grams of the styrene was added to 150 ml. of distilled water, 0.3 g. of potassium persulfate and 2 ml. of Tergitol No. 4. After a reaction period of twelve hours, the polymer was precipitated by pouring the emulsion into 300 ml. of 10% sodium chloride solution. The polymer was filtered and washed with water. After reprecipitating the polymer from an acetone solution by dilution with methanol, the solid polymer was dried for twenty-four hours at 70°.

Molecular Weights of Polymers.—The average molecular weights of the polymers were determined by the viscosity method.[9] A mixed solvent (100 ml. of benzene with 150 ml. of acetone) was used and the equation constants ($K = 3.57 \times 10^{-4}$, $a = 0.67$) were determined using samples of polystyrene of known average molecular weight.

Summary

1. The preparation of nine new trifluoromethyl- and chloro-(trifluoromethyl)-substituted styrenes is described.
2. Polymers of these styrenes were prepared and their average molecular weights determined.
3. It was found that substituted bromobenzenes in which a chlorine is ortho to a bromine do not react with magnesium in ether while those in which the chlorine is in a position other than ortho readily form a Grignard reagent.

LAFAYETTE, IND. RECEIVED[10] MARCH 30, 1950

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[9] A. Weissberger, "Physical Methods of Organic Chemistry," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1945, pp. 144–146.

[10] Original manuscript received October 24, 1949.

[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Isomerization of Saturated Hydrocarbons. VII.[1] The Effect of Light upon the Isomerization of Methylcyclopentane in the Presence of Aluminum Bromide–Hydrogen Bromide

BY HERMAN PINES, EUGENE ARISTOFF[2] AND V. N. IPATIEFF

It has been shown previously[3,4] that under certain controlled conditions aluminum bromide–hydrogen bromide did not cause the isomerization of *n*-butane to isobutane or methylcyclopentane to cyclohexane unless traces of olefins or alkyl halides were present. In order to explain the function of the traces of olefins a chain mechanism has been proposed[5] in which it was suggested that the olefins reacted with the hydrogen halide to form the corresponding alkyl- or cycloalkyl halide which in the presence of aluminum bromide reacted with the saturated hydrocarbon such as methylcyclopentane to form cyclohexane.

This study has been extended in order to determine whether the isomerization of methylcyclopentane can proceed without the addition of the above mentioned types of chain initiator. The reaction was conducted in the presence of ultraviolet light; it was assumed that under these conditions the hydrogen bromide will undergo a partial dissociation into a hydrogen and a bromine atom and the latter then will react with methylcyclopentane to form the corresponding bromide. It was found that isomerization proceeded when a reaction tube containing methylcyclopentane, aluminum bromide and hydrogen bromide in a molal ratio of approximately 100:2:1, was exposed for nine hours to a quartz cadmium–mercury vapor arc lamp. The degree of isomerization of methylcyclopentane to cyclohexane was increased from 18 to 24% when quartz instead of a Pyrex reaction tube was used. In the absence of hydrogen bromide, even after eighteen hours of irradiation, isomerization did not occur (Table I). The appearance of the reaction mixture before and after exposure to ultraviolet did not change; the solution was homogeneous and colorless. In two experiments (5 and 7) the small amounts of non-condensable gases produced during the reaction were collected and analyzed by a mass spectrometer[6]; the gases contained over 97% of hydrogen.

The results obtained are in accordance with the proposed chain mechanism of isomerization,[5] which can be presented as

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[1] For paper VI of this series see H. Pines, E. Aristoff and V. N. Ipatieff, THIS JOURNAL, 71, 749 (1949).

[2] Universal Oil Products Company Predoctorate Research Fellow 1947–1949.

[3] H. Pines and R. C. Wackher, THIS JOURNAL, 68, 585, 2518 (1946).

[4] H. Pines, B. M. Abraham and V. N. Ipatieff, *ibid.*, 70, 1742 (1948).

[5] H. S. Bloch, H. Pines and L. Schmerling, *ibid.*, 68, 153 (1946).

[6] The analysis of the gases on a mass spectrograph was made by Mr. Joseph Grutka at the Laboratory of the Universal Oil Products.