The reducing action of *t*-butylmagnesium chloride[3] on di-(*p*-chlorophenyl)-acetyl chloride did give the ethanol as a colorless crystalline solid, m.p. 98.5–99.5°, in 27% yield

$$(p\text{-ClC}_6\text{H}_4)_2\text{CH—COCl} + 2t\text{-C}_4\text{H}_9\text{MgCl} \longrightarrow$$
$$(p\text{-ClC}_6\text{H}_4)_2\text{CH—CH}_2\text{OMgCl} + 2i\text{-C}_4\text{H}_8 + \text{MgCl}_2$$

Acid-catalyzed dehydration of the ethanol was accompanied by rearrangement and the product was *p,p'*-dichlorostilbene. Both DMC and the new isomer (*i*-DMC) have an ultraviolet absorption maximum at 226 mμ; the primary alcohol absorbs more strongly (Table I).

TABLE I

ULTRAVIOLET ABSORPTION SPECTRA OF DMC AND *i*-DMC[a]

Wave length (mμ)	Specific extinction DMC	Specific extinction *i*-DMC
220	79.0	77.0
226	80.0	91.3
230	67.0	87.5
234	34.0	39.4
240	10.8	8.2
250	3.0	4.3
270	2.5	5.8

[a] Determined in isoöctane solution with a Beckman model DU ultraviolet spectrophotometer.

Insecticidal tests with red spiders, two spotted mites, house flies, German roaches, webbing clothes moths, pea aphids, milkweed bugs, Southern armyworms and Mexican bean beetle larvae showed low or no activity for the β,β-di-(*p*-chlorophenyl)-ethanol.[4] Therefore, a necessary structural feature for activity in the DMC type of compound is probably the oxidized tertiary carbon atom in the diarylalkylmethane: $\text{Ar}_2\text{C(OH)R}$.

Experimental

***p,p'*-Dichlorobenzhydrylmagnesium Chloride Plus Formaldehyde.**—A solution of 27.0 g. (0.1 mole) of di-(*p*-chlorophenyl)-chloromethane[5] in 150 ml. of ether was added to 2.4 g. (0.1 atom) of magnesium and 40 ml. of ether in the usual three-necked flask apparatus during one hour while a stream of formaldehyde was led to the surface of the Grignard reagent. Formaldehyde was generated from 15 g. (0.5 mole formaldehyde) of trioxane (du Pont) and 0.75 g. of anhydrous zinc chloride by heating the mixture at 80–85° in a stream of dry nitrogen. After the addition of the chloride and formaldehyde the mixture was stirred for one hour and then hydrolyzed with 25 g. of ammonium chloride in 150 ml. of ice and water. Collecting the precipitate and washing with water gave 10 g. (40% yield) of *sym*-tetra-(*p*-chlorophenyl)-ethane, which decomposed at 300–325° with the formation of a red color.[5] The ether layer from the hydrolysis gave some unreacted chloride and *p,p'*-dichlorobenzhydrol, but no *i*-DMC could be isolated.

β,β-Di-(*p*-chlorophenyl)-ethanol.—*t*-Butylmagnesium chloride in ethyl ether (2.3 molar) was made in 77% yield.[6] This was diluted with ether to give 150 ml. containing 0.23 mole, placed in the usual three-necked flask apparatus, and 14.6 g. (0.049 mole) of di-(*p*-chlorophenyl)-acetyl chloride[7] in 75 ml. of ether was added during 2.5 hours while the reaction mixture was gently refluxed. After 0.5 hour additional refluxing the ether solution was hydrolyzed with 13.5 g. of ammonium chloride in 150 ml. of ice and water. The ether layer yielded 11.5 g. of waxy solid which on crystallization from benzene gave 5.1 g. (39%) of crude ethanol melting 93–95°. Several crystallizations from benzene–Skellysolve B and finally from alcohol–water raised the melting point to 98.5–99.5°.

Anal. Calcd. for $\text{C}_{14}\text{H}_{12}\text{Cl}_2\text{O}$: Cl, 26.6; OH, 6.35. Found: Cl, 26.4; OH, 6.18.[8]

Di-(*p*-chlorophenyl)-acetyl chloride was previously reported as an oil which did not crystallize at 0° and which decomposed on vacuum distillation at 3–4 mm.[7] The material used here melted 34.5–35.0° as the result of purifying by high vacuum distillation (140–150° at 0.1 mm.) from a short path pot still and washing the partially solidified distillate with Skellysolve A. Crystallization from the filtrate gave additional solid. The total recovery of purified acid chloride from the crude was about two-thirds which melted above 28°.[9]

Anal. Calcd. for $\text{C}_{14}\text{H}_9\text{Cl}_3\text{O}$: Cl, 35.4. Found: Cl, 35.0.

The 3,5-dinitrobenzoate derivative of *i*-DMC was made in pyridine from 3,5-dinitrobenzoyl chloride in the usual way[10]; m.p. 149–150°.

Anal. Calcd. for $\text{C}_{21}\text{H}_{14}\text{Cl}_2\text{N}_2\text{O}_6$: N, 6.08. Found: N, 5.82.

***p,p'*-Dichlorostilbene from β,β-Di-(*p*-chlorophenyl)-ethanol.**—A mixture of 50 mg. of the ethanol and 50 mg. of sodium bisulfate was heated in a microsublimation apparatus for 10 hours at 110–130°. When a vacuum of 1 mm. was applied, 20 mg. of crude product sublimed. Crystallization from ethanol gave 10 mg. (20%) melting 173–174°. A mixed melting point with authentic *p,p'*-dichlorostilbene gave 170–173°.

Refluxing a solution of 0.1 g. of ethanol and 0.5 g. of phosphorus pentoxide in 5 ml. of benzene for one hour, washing with water and evaporating the benzene failed to effect dehydration.[11]

The authentic stilbene was made by the thermal decomposition of di-(*p*-chlorophenyl)-fumarate at 250–255°. After 18 hours heating carbon dioxide was no longer given off. Crystallization from ethanol gave a product melting 172–173°.[12]

Di-(*p*-chlorophenyl)-fumarate, m.p. 174–176°, was made from *p*-chlorophenol and fumaryl chloride.[13]

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[3] F. C. Whitmore, *et al.*, THIS JOURNAL, **63**, 643 (1941).

[4] George S. Kido, unpublished results, Wisconsin Alumni Research Foundation, Madison, Wisconsin.

[5] P. J. Montagne, *Rec. trav. chim.*, **25**, 379 (1906).

[6] F. C. Whitmore and A. L. Houk, THIS JOURNAL, **54**, 3714 (1932).

[7] O. Grummitt and D. Marsh, *ibid.*, **71**, 4156 (1949).

[8] M. Freed and A. M. Wynne, *Ind. Eng. Chem.*, *Anal. Ed.*, **8**, 278 (1936).

[9] D. Marsh of this Laboratory carried out the purification.

[10] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," 3rd edition, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 165.

[11] M. S. Kharasch and H. G. Clapp, *J. Org. Chem.*, **3**, 355 (1938).

[12] R. Kade, *J. prakt. Chem.*, [2] **19**, 461 (1879).

[13] R. Anschutz, *Ber.*, **60**, 1320 (1927).

SHERWIN-WILLIAMS LABORATORY
WESTERN RESERVE UNIVERSITY
CLEVELAND 6, OHIO

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Preparation of Some Aromatic Sulfonyl Fluorides

BY BERNARD I. HALPERIN, MELVIN KRSKA, EDWARD LEVY AND CALVIN A. VANDERWERF

The method reported by Ferm and VanderWerf[1] for the synthesis of aromatic sulfonyl fluorides[2] by addition of sodium nitrite to a solution of the corresponding sulfonamide in anhydrous hydrogen fluoride has been extended by the preparation of the following compounds in the yields indicated: benzenesulfonyl fluoride (53%), *m*-nitrobenzenesulfonyl fluoride (64%) and *o*-toluenesulfonyl fluoride (78%).

Attempted preparation of acyl fluorides by the same method was unsuccessful, only starting amide

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[1] R. L. Ferm and C. A. VanderWerf, THIS JOURNAL, **72**, 4809 (1950).

[2] These compounds, as well as acyl fluorides, are usually prepared by treatment of the corresponding chlorides with fluorosulfonic acid or with aqueous solutions of inorganic fluorides. See W. Steinkopf, German Patent 497,242, Feb. 22, 1927 [*C. A.*, **24**, 3516 (1930)]; W. Davies and J. H. Dick, *J. Chem. Soc.*, 2104 (1931); A. I. Mashentsev, *J. Applied Chem.* (*U. S. S. R.*), **20**, 854 (1947).

and the corresponding acid being obtained even when the reaction and isolation were carried out without the addition of water at any stage.

Experimental

The benzenesulfonyl fluorides were prepared by the slow addition during the course of one hour of 0.30 mole of sodium nitrite to a solution of 0.25 mole of the benzene sulfonamide in 5.5 moles of anhydrous hydrogen fluoride contained in a monel metal flask at a temperature slightly above 0°. The mixture was stirred for an additional hour in an ice-bath and then decomposed with steam at about 80°, until evolution of gas had ceased. The contents were poured into a stainless steel beaker containing 200 g. of ice. The resulting oily layer was separated and taken up in 200 ml. of ether. The ether solution was washed with water, dried over anhydrous magnesium sulfate, the ether removed by distillation, and the residue distilled at a pressure of 2 mm.

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DEPARTMENT OF CHEMISTRY
UNIVERSITY OF KANSAS
LAWRENCE, KANSAS

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The Preparation of β-Nitropropanoic Acid

BY H. B. HASS,[1] H. FEUER AND S. M. PIER

In a recent patent[2] "Preparation of Substituted Acids From Lactones," it is stated that "the reaction of β-propiolactone with sodium nitrite produces principally β-nitropropanoic acid, some of the nitrate also probably being formed." However, no conditions for this reaction are given.

We have obtained a 35% yield of β-nitropropanoic acid when β-propiolactone was added slowly to an aqueous solution of sodium nitrite. Variations in the molar ratios of lactone and salt did not effect the yield. No nitrite or nitrate was isolated from the reaction mixture. The reaction of the lactone with nitrogen tetroxide under anhydrous conditions resulted only in a partial polymerization of the lactone.

Experimental

One-fourth mole (18 g.) of β-propiolactone was added dropwise during 15 minutes to 25 g. (0.35 mole) of sodium nitrite dissolved in 50 ml. of water in a three-neck flask equipped with stirrer, thermometer and dropping funnel. The reaction mixture was kept at 15–20° by use of a cold water-bath. Stirring was continued 4 hours after the addition was completed. The resulting clear, red solution was cooled to −5°, in an erlenmeyer flask, ether was added and 85% phosphoric acid dropped in until the solution was acid to litmus. During the acidification step the ether was frequently decanted and fresh ether added. The combined ether extracts were dried with Drierite and the ether evaporated. The orange-red oil remaining was frozen and allowed to thaw on a suction filter and a white solid remained behind. Repetition of the crystallization gave a total of 9.5 g. (35%) of white solid. Recrystallization from benzene or chloroform yielded white needles, m.p. 66°; lit. value 66°.[3,4]

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[1] General Aniline and Film Corp., New York, N. Y.

[2] T. L. Gresham, U. S. Patent 2,449,987 (1948).

[3] I. M. Heilbron, "Dictionary of Organic Compounds," Eyre and Spottiswoode, London, 1943, Vol. III, p. 238.

[4] Financial Support of this research was supplied by the United States Office of Naval Research.

DEPARTMENT OF CHEMISTRY AND
PURDUE RESEARCH FOUNDATION
PURDUE UNIVERSITY
LAFAYETTE, INDIANA

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The Reaction of Methylamine with Nitroaminoguanidine

BY RONALD A. HENRY AND G. B. L. SMITH

The dearrangement of nitroaminoguanidine in a solution of ammonium carbonate was shown previously[1] to yield hydrazine, guanidine, nitroguanidine, aminoguanidine and diaminoguanidine. The hydrazinolysis of nitroaminoguanidine also gives diaminoguanidine.[2] The reaction of methylamine with nitroaminoguanidine in aqueous solution has now been studied and is analogous to these other reactions. The principal products isolated and identified were 1-methyl-3-nitroguanidine, 1-methyl-3-aminoguanidine, 1,3-diaminoguanidine and 1-methyl-2-amino-3-nitroguanidine. Minor amounts of triaminoguanidine and other unidentified compounds were also isolated as derivatives. Although 1,3-dimethyl-2-aminoguanidine and 1,3-dimethylguanidine could also theoretically be formed, they were not among the products; the former compound has been prepared by the hydrazinolysis of N,N′,S-trimethylisothiourea iodide.

1-Methyl-1-amino-3-nitroguanidine has been prepared by the reaction of methylhydrazine and 1-methyl-1-nitroso-3-nitroguanidine, using a method developed by McKay and Wright.[3]

Experimental[4]

Methylamine with Nitroaminoguanidine.—To a solution of 23.8 g. (0.2 mole) of nitroaminoguanidine and 24.0 g. of potassium hydroxide in 60 ml. of water at 30° was added, all at once, 27.0 g. (0.4 mole) of methylamine hydrochloride. While the resulting viscous solution was stirred, the temperature was raised to 60° during 5 minutes and maintained there for 25 minutes. The reaction mixture was then cooled to 0°, neutralized with concentrated hydrochloric acid, and stored for 4 days at 0°. The solid material (5.6 g.), which separated, was removed by filtration, washed with 10 ml. of cold water and dried (A); the mother liquors were retained (B).

(A) When the solid material was extracted with one 25-ml. and two 10-ml. portions of hot absolute ethanol, about 4.5 g. of potassium chloride was left. From the alcoholic extract there was recovered 0.02 g. of unreacted nitroaminoguanidine (dec. 182–183°) and 0.5 g. of 1-methyl-3-nitroguanidine (2.2%), melting at 159° after one recrystallization from 3 ml. of ethanol. A mixed melting point with an authentic specimen of methylnitroguanidine was 160°.

By treating the final alcoholic mother liquors with benzaldehyde and picric acid there was occasionally obtained a small quantity of very fine yellow needles, decomposing at 230–231° (depends on the rate of heating). A mixed melting point with a sample of tribenzaltriaminoguanidine picrate (m.p. 227°) was 227° (dec.). An X-ray powder pattern was also the same as that for tribenzaltriaminoguanidine picrate.

Anal. Calcd. for $C_{28}H_{23}N_9O_7$: C, 56.28; H, 3.88; N, 21.10. Found: C, 56.20; H, 3.83; N, 21.33.

In one experiment in which the original reaction mixture was evaporated to a small volume before cooling, there was isolated, in addition to the above compounds, about 0.3 g. of a compound which decomposed at 191–193° after recrystallization from water. This compound in an acid solution reduced potassium iodate very slowly indicating a protected hydrazino group. It was analyzed but not identified.

Anal. Found: C, 15.10, 15.05; H, 3.66, 3.41; N, 53.69.

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[1] R. A. Henry and G. B. L. Smith, THIS JOURNAL, **71**, 1872 (1949).

[2] R. A. Henry, H. D. Lewis and G. B. L. Smith, *ibid.*, **72**, 2015 (1950).

[3] A. F. McKay and G. F. Wright, *ibid.*, **69**, 3028 (1947); A. F. McKay, *ibid.*, **71**, 1968 (1948).

[4] All melting points have been corrected against known standards.