wave length examined, with the possible exception of 2894 Å.

3. The activation by 2894 Å. appears to be intermediate between that of 2967 Å. and the other wave lengths tested.

4. No demonstrable antirachitic properties were produced by irradiation of 7-dehydrocholesterol in ether by ultraviolet of 3130 Å.

5. The superior effectiveness of 2967 Å. in antirachitic activation of 7-dehydrocholesterol parallels the significant superiority of this wave length in inducing healing upon direct irradiation of depilated rachitic rats, which supports the hypothesis that 7-dehydrocholesterol is a significant precursor of vitamin D in the skin.

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[CONTRIBUTION NO. 211 FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Identification of Organic Compounds. I. Chlorosulfonic Acid as a Reagent for the Identification of Aryl Halides

BY ERNEST H. HUNTRESS AND FREDERICK H. CARTEN[1,2]

Although the action of chlorosulfonic acid has been studied upon many compounds, either as a means of introducing the sulfonic acid group or the chlorosulfonyl group, no systematic attempt to employ it as a reagent for the identification of organic compounds has been reported. The present paper reports the study of chlorosulfonic acid as applied to the identification of a considerable number of halogenated aromatic hydrocarbons.

The object of this work was to find a set of standard conditions such that treatment of the sample with chlorosulfonic acid would yield readily the corresponding arylsulfonyl chloride which in turn could be converted to the corresponding sulfonamide. The process of introducing the $-SO_2Cl$ group is hereafter designated as "chlorosulfonylation."

Two standard procedures (I and II) for effecting chlorosulfonylation have been devised and tested upon a large number of compounds. The first carries out the chlorosulfonylation in chloroform solution; the second uses no solvent. Both procedures employ a relatively large excess of chlorosulfonic acid in order to convert the intermediate sulfonic acid (to be expected from one mole of chlorosulfonic acid) as completely as possible to the corresponding sulfonyl chloride. The yields of arylsulfonyl chloride thus obtained are generally high (60–90%) and the process is extremely simple to execute.

Conversion of the arylsulfonyl chloride thus obtained to the corresponding arylsulfonamide was effected either by treatment with concentrated aqueous ammonium hydroxide, or by reaction with solid ammonium carbonate. The yields on this step were invariably nearly quantitative.

In a few cases the reaction with chlorosulfonic acid yielded abnormal products. Thus fluorobenzene, iodobenzene, *o*-dichlorobenzene and *o*-dibromobenzene at 50° with chlorosulfonic acid in the absence of any solvent, chloroform, yielded the corresponding sulfones. In a few other instances a small amount of the corresponding sulfones accompanied the usual sulfonyl chloride. From the point of view of identification, however, these sulfones serve just as well as the sulfonyl chlorides. Furthermore, in those cases where they accompany the sulfonyl chloride, they are readily separable from the final sulfonamide by their insolubility in alkali, the sulfonamides readily dissolving and being reprecipitable on acidification.

Another abnormal type of reaction occasionally observed was nuclear chlorination. This occurred notably with *p*-diiodobenzene and 1,2,4,5-tetrachlorobenzene but does not interfere with the identification of these compounds since the substitution products are readily obtained and have characteristic melting points.

Unsatisfactory results were obtained with the following compounds: *o*-chloroiodobenzene, *p*-chloroiodobenzene, *m*-chloroiodobenzene, *o*-bromoiodobenzene, *p*-bromoiodobenzene, *o*-iodotoluene, *m*-iodotoluene and *p*-iodotoluene. Treatment

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(1) This paper is constructed from part of a dissertation submitted by Frederick H. Carten to the Faculty of the Massachusetts Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy in June, 1939.

(2) This work was assisted by a grant from the Warren Fund of the American Academy of Arts and Sciences for which grateful acknowledgment is hereby made.

of *o*- and of *p*-chlorobiphenyl by either procedure I or II gave only water soluble products.

Of the 28 sulfonamides reported in Table I six are new. The structures assigned in these six cases are, therefore, tentative and are based on analogies with other compounds actually studied. Of the four sulfones described two are previously unreported. The tentative structures assigned to these are, therefore, based only on analogies, and their complete establishment was not attempted in this research.

Since the three isomeric trichlorobenzenes yield sulfonamides which are not well adapted for their positive identification, we have studied the utility of nitration for this purpose. All of the mono- and dinitro derivatives of these three compounds have been reported but by such diversified procedures that we have devised a set of standard conditions for nitration. The dinitration products serve conveniently for characterization of the trichlorobenzenes, confirmatory evidence being supplied by their reaction with aniline.

Experimental Work

The melting points reported in this paper are uncorrected. They were determined on a standard rod form 360° melting point thermometer in a copper melting point block of the Berl and Kullmann type. Observation of the sample was assisted by means of a small 25 power microscope permanently attached to the apparatus.

The chlorosulfonic acid used in this work was obtained by distilling Eastman Kodak Co. practical grade in a stream of hydrogen chloride, retaining only the portion distilling between 153–157° (92% of the original material).

The organic compounds were carefully purified until their melting or boiling points checked closely with the values accepted in the literature.

Chlorosulfonylation with Chlorosulfonic Acid

Procedure I.—The compound (1.0 g.) was dissolved in chloroform (5 cc.), the solution placed in a six-inch (15 cm.) test-tube resting in an ice-bath at 0°, and treated dropwise with chlorosulfonic acid (5.0 g.). After the initial evolution of hydrogen chloride had subsided, the reaction mixture was brought to room temperature. After about twenty minutes the contents of the tube were poured into a 50-cc. beaker filled with crushed ice, the chloroform layer separated and washed with cold water, and the solvent evaporated. The residual crude arylsulfonyl chloride was then recrystallized from dry low boiling petroleum ether or from chloroform and dried in vacuum over concentrated sulfuric acid.

Procedure II.—This was exactly like Procedure I except that no solvent was employed. After pouring the sirupy reaction mixture onto crushed ice, the resultant arylsulfonyl chloride or sulfone was filtered with suction if a solid, or separated by means of a small separatory funnel if a liquid, washed with water and recrystallized from low boiling petroleum ether or benzene.

Some of the aryl halides used in this work react but slowly with chlorosulfonic acid at room temperature. Deviations from the above standard procedures found to result in improved yields are noted under the individual descriptions.

Every arylsulfonyl chloride described in this report when dissolved in alcohol and boiled with solid ammonium thiocyanate gives (on cooling) a yellow amorphous precipitate. The precise nature of the reaction is unknown but it serves as a qualitative means of detection of the sulfonyl chloride group. Our use of it represents an extension of the observations of Remsen and Turner,[3] on the reaction of benzenesulfonyl chloride.

Conversion of Arylsulfonyl Chlorides to Sulfonamides

Procedure A.—The arylsulfonyl chloride (0.5 g.) prepared according to Procedures I or II was boiled for ten minutes with concentrated (sp. gr. 0.90) ammonium hydroxide (5 cc.). After cooling to room temperature, and adding cold water (10 cc.), the resultant solid sulfonamide was filtered with suction and thoroughly washed. It was then recrystallized to constant melting point from dilute ethanol and dried at 105°.

Procedure B.—The product from either of the chlorosulfonylation procedures I or II (0.5 g.) was mixed with dry powdered ammonium carbonate (2.0 g.) and heated at 100° for thirty minutes. After washing with several 10-cc. portions of cold water, the residual solid was filtered off and recrystallized from dilute ethanol.

Remarks.—Any sulfone which may have been formed by the action of chlorosulfonic acid in Procedures I or II is of course entirely unaffected by either ammonium hydroxide or ammonium carbonate in Procedure A or B. It may be separated from the corresponding aryl sulfonamide by virtue of its insolubility in cold 6 *N* sodium hydroxide. The sulfonamides dissolve in the alkali and after filtration of the inert sulfone may be reprecipitated by addition of 6 *N* hydrochloric acid.

Sulfones Obtained with Chlorosulfonic Acid.—In four cases application of Procedure II to the original aryl halide gave only sulfones in 71–74% yield. Thus, fluorobenzene gave 4,4'-difluorodiphenylsulfone, white needles from benzene, m. p. 97–98 uncor. This product was obtained in 100% yield by heating the reaction mixture at 40° for one hour.

Anal. Calcd. for $C_{12}H_8F_2O_2S$: C, 56.70; H, 3.15. Found: C, 56.43, 56.82; H, 3.38, 3.54.

Iodobenzene by either Procedure I or II gave 4,4'-diiododiphenylsulfone, needles from benzene or glacial acetic acid, m. p. 201–202°.

Anal. Calcd. for $C_{12}H_8I_2O_2S$: S, 6.81; I, 53.99. Found: S, 6.92, 6.86; I, 53.93, 53.71.

The compound is undoubtedly identical with the so-called x,x-diiododiphenylsulfone of Beilstein VI-336.[4] From *o*-dichlorobenzene, Procedure II yielded 3,4,3',4'-tetrachlorodiphenylsulfone, accompanied by a small pro-

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[3] Remsen and Turner, *Am. Chem. J.*, **25**, 198 (1901).

[4] Willgerodt and Waldmeyer, *J. prakt. Chem.*, (2) **59**, 195 (1899).

TABLE I

SULFONYL CHLORIDES AND SULFONAMIDES

Original	Resultant sulfonyl chloride[a,d] Isomer obtd.	M. p., °C. uncor.	Corresponding sulfonamide[b,c,d] M. p., °C. uncor.
A. Benzene series (—SO_2Cl or —SO_2NH_2-1)			
F	4-F	35–36	124–125
Cl	4-Cl	53.5	142–143
Br	4-Br	75.4	161.5
1,2-diCl	3,4-diCl	18–19[e]	134–135
1,3-diCl	2,4-diCl	52–53	179–180[g]
1,4-diCl[f]	2,5-diCl	38	179.5–180[g]
1,2-diBr	3,4-diBr[h]	31–34	175–176
1,3-diBr	2,4-diBr	78–79	188–189
1,4-diBr[f]	2,5-diBr	71	194–195
1-CH_3, 2-F	3-CH_3, 4-F	oil	104–105
1-CH_3, 3-F[i]	2-CH_3, 4-F	oil	172–173
1-CH_3, 4-F[i]	2-CH_3, 5-F	oil	140–141
1-CH_3, 2-Cl	3-CH_3, 4-Cl	63	126
1-CH_3, 3-Cl[i]	2-CH_3, 4-Cl	52–53	184–185
1-CH_3, 4-Cl[i]	2-CH_3, 5-Cl	21	142–143
1-CH_3, 2-Br	3-CH_3, 4-Br	59–60	145–146
1-CH_3, 3-Br[i]	2-CH_3, 4-Br	49–50	167–168
1-CH_3, 4-Br[i]	2-CH_3, 5-Br	33–35	164–165
1-CH_3, 2,4-diCl[i]	2,4-di-Cl, 5-CH_3	71–72	175–176
1-CH_3, 2,6-diCl[i]	2,4-di-Cl, 3-CH_3	54–56	199–201
1,2,3-triCl[j]	2,3,4-triCl	64–65	226–230 dec.
1,2,4-triCl[k]	2,4,5-triCl	31–34	>200
1,3,5-triCl[l]	2,4,6-triCl	35–40	210–212 dec.
1,3,5-triBr	2,4,6-triBr	58–60	220–222 dec.
B. Naphthalene series (—SO_2Cl or —SO_2NH_2-1)			
1-Cl	4-Cl	92–93	185–186
2-Cl	7-Cl	124–126	231–232
1-Br	4-Br	81–83	191–193
2-Br	7-Br	142–143	207–208

[a] Except for those from fluorobenzene and chlorobenzene which were recrystallized from benzene and ether, respectively, all other sulfonyl chlorides were recrystallized from petroleum ether. [b] All sulfonamides were recrystallized from dilute alcohol. [c] All sulfonamides were analyzed for nitrogen (or halogen in two cases) and gave results in excellent accord with the theoretical values. [d] In order to save space references to m. p.'s previously reported are not included. [e] Accompanied by 8% of the corresponding sulfone. [f] Does not react at room temperature but gives 80% yield on refluxing for one hour. [g] The m. p. of a mixture of these two compounds was depressed to 168–171°. [h] Accompanied by 3% of the corresponding sulfone. [i] Followed by heating at 50° for ten minutes. [j] Followed by heating at 80° for one hour. [k] Followed by heating at 150° for one hour. [l] Followed by heating at 150° for thirty minutes.

portion (3–4%) of 3,4-dichlorobenzenesulfonamide. The sulfone crystallizes in plates from absolute alcohol or glacial acetic acid, m. p. 175–176° uncor.

Anal. Calcd. for $C_{12}H_6Cl_4O_2S$: S, 9.00; Cl, 39.85. Found: S, 8.76, 9.00; Cl, 39.65, 39.57.

It is undoubtedly identical with the so-called bis-[x,x'-dichlorophenyl]-sulfone (Beilstein VI-330).[5] From *o*-dibromobenzene Procedure II yielded 3,4,3',4'-tetrabromodiphenylsulfone, plates from hot alcohol, m. p. 176–177°.

Anal. Calcd. for $C_{12}H_6Br_4O_2S$: Br, 59.87. Found: Br, 60.66, 60.96.

Chlorosulfonic acid gave "abnormal" results in three cases.

2,3,5,6-Tetrachloro-1,4-diiodobenzene: from *p*-diiodobenzene heated to 50° for five minutes with five parts of chlorosulfonic acid. Vigorous evolution of sulfur dioxide occurred and a pale brown solid precipitated. After pouring onto ice the crude product recrystallized from absolute alcohol or from glacial acetic acid in long white needles, m. p. 210–211° uncor.

Anal. Calcd. for $C_6Cl_4I_2$: Cl, 30.32; I, 54.27. Found: Cl, 30.42, 29.69; I, 52.12, 52.12.

Hexachlorobenzene: from 1,2,4,5-tetrachlorobenzene (5.0 g.) refluxed with chlorosulfonic acid (20.0 g.) for one hour. During this period, the reaction mixture turned dark green and a white solid appeared on its surface. As this solid gradually sublimed into the condenser its solution in the condensing chlorosulfonic acid was deep red, changing to green upon striking the mixture in the flask. After cooling, and pouring onto ice, the separating white solid (5.2 g., 78%) recrystallized from petroleum ether as needles, m. p. 218–219° uncor., and failed to depress the melting point of an authentic sample of hexachlorobenzene.

Anal. Calcd. for C_6Cl_6: Cl, 74.70. Found: Cl, 74.35, 74.29.

2-Bromo-5-chlorobenzenesulfonamide: from *p*-chlorobromobenzene by refluxing for one hour with five times its weight of chlorosulfonic acid, pouring onto ice and converting the resultant sulfonyl chloride (86% yield, m. p. 40–42°) to amide via Procedures A or B. The product showed m. p. 189–190° uncor.

Anal. Calcd. for $C_6H_5BrClNO_2S$: N, 5.18. Found: N, 5.23, 5.27.

The chlorosulfonylation of *p*-bromochlorobenzene could yield either 2-bromo-5-chlorobenzenesulfonyl chloride or 2-chloro-5-bromobenzenesulfonyl chloride or both. Armstrong and Briggs[6] report melting points of 46 and 66°, respectively, for these two isomers and melting points of 191 and 178° for the respective corresponding sulfonamides. Moreover, they report that the two sulfonamides are isomorphous and that their mixture showed no depression of melting point. This indicates that in our experiments both isomers may be formed but that our final product is mainly 2-bromo-5-chlorobenzenesulfonamide.

Nitration of the Trichlorobenzenes.—One gram of the compound was dissolved in five grams of fuming nitric acid (d = 1.49). 1,2,3-Trichloro- and 1,2,4-trichlorobenzene dissolved promptly with evolution of heat; 1,3,5-trichlorobenzene required warming for fifteen minutes on the water-bath. After complete solution had occurred, the mixture was poured onto crushed ice, the solid filtered and recrystallized from alcohol; yield quantitative. By this procedure 1,2,3-trichlorobenzene yielded 2,3,4-trichloro-1-nitrobenzene, m. p. 55–56°; 1,2,4-trichlorobenzene yielded 2,4,5-trichloro-1-nitrobenzene, m. p. 56°; and 1,3,5-trichlorobenzene gave 2,4,6-trichloro-1-nitrobenzene, m. p. 67–68°.

Dinitration.—To the nitric acid solution of mononitro compound obtained above was added 5 g. of concentrated sulfuric acid and the mixture refluxed for one hour. After cooling the mixture was poured into 100 cc. of water

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(5) Friedel and Crafts, *Ann. chim.* (6) **10**, 415 (1887).

(6) Armstrong and Briggs, *Chem. News*, **65**, 138–139 (1892).

and the precipitated dinitrotrichlorobenzene filtered, washed and recrystallized from alcohol; yields quantitative. By this procedure 1,2,3-trichlorobenzene yielded 4,5,6-trichloro-1,3-dinitrobenzene, m. p. 92–93°; 1,2,4-trichlorobenzene yielded 2,4,5-trichloro-1,3-dinitrobenzene, m. p. 102.5–103.5°; and 1,3,5-trichlorobenzene gave 2,4,6-trichloro-1,3-dinitrobenzene, m. p. 128.5°.

Reaction of the Dinitrotrichlorobenzenes with Aniline.—One gram of the dinitrotrichlorobenzene and five grams of pure aniline were heated on a water-bath for one hour. The mixture was then cooled and extracted with successive portions of 6 *N* hydrochloric acid to remove excess aniline. After filtering off the residual solid and washing with water, it was recrystallized from benzene or ethyl alcohol.

Application of this procedure to the dinitration product from 1,2,3-trichlorobenzene gave 4,6-dianilino-5-chloro-1,3-dinitrobenzene, m. p. 136–138°.

Anal. Calcd. for $C_{18}H_{13}ClN_4O_4$: N, 14.56. Found: N, 14.88, 14.91.

From the dinitration product of 1,2,4-trichlorobenzene there resulted 2,6-dianilino-5-chloro-1,3-dinitrobenzene, m. p. 182°.

Anal. Calcd. N, 14.56; Cl, 9.21. Found: N, 14.79, 14.86; Cl, 9.20, 9.28.

From the dinitration product of 1,3,5-trichlorobenzene there was obtained the previously reported 2,4,6-trianilino-1,3-dinitrobenzene, m. p. 179–180°.

Summary

1. A method for the identification of aryl halides by means of chlorosulfonylation with chlorosulfonic acid has been shown to yield excellent results.

2. Of thirty-two aryl halides studied, thirty yield characteristic arylsulfonyl chlorides readily converted to the corresponding arylsulfonamides and the other two yield reaction products characteristic of the original compound.

3. Three trichlorobenzenes have been characterized by mono-, di- and tri-nitration and the reaction products of the dinitrotrichlorobenzenes with aniline have been found useful derivatives.

CAMBRIDGE, MASS. RECEIVED AUGUST 17, 1939

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

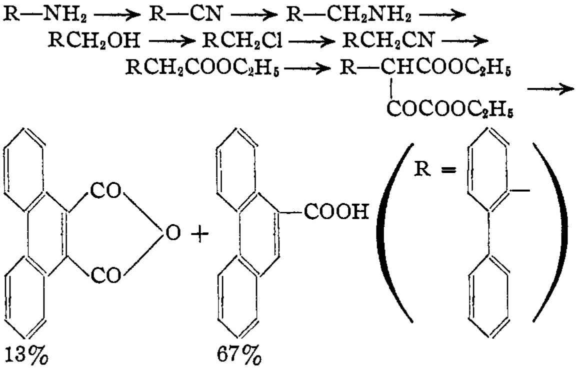
A New Synthesis of Phenanthrene Derivatives. I. Phenanthrene-9,10-dicarboxylic Anhydride and Phenanthrene-9-carboxylic Acid

BY T. A. GEISSMAN AND ROY W. TESS

In an attempt to develop a convenient method for the synthesis of phenanthrene-9,10-dicarboxylic anhydride, a modification of the Bougault method of ring closure[1] applied to the biphenyl ring system has been studied. While the results obtained are encouraging, those described in this paper are of a preliminary nature, and are published at this time because of the necessity for temporarily suspending work on the problem.

A new approach to the synthesis was sought for two reasons: the method used appeared to offer (1) a cheaper procedure and one more readily adapted to the preparation of large amounts than those of Jeanes and Adams[2] or of Weizmann, Bergmann and Berlin,[3] and (2) a synthesis which could be generalized more readily than either of those mentioned[4] to the preparation of analogous compounds containing other substituents in the rings.

The steps in the synthesis are



$$R{-}NH_2 \longrightarrow R{-}CN \longrightarrow R{-}CH_2NH_2 \longrightarrow RCH_2OH \longrightarrow RCH_2Cl \longrightarrow RCH_2CN \longrightarrow RCH_2COOC_2H_5 \longrightarrow \underset{\displaystyle COCOOC_2H_5}{R{-}\underset{|}{C}HCOOC_2H_5} \longrightarrow$$

The synthesis proceeds smoothly in the manner shown, and although suspension of the study has made it impossible to work out conditions for a quantitative ring-closure without decarboxylation, the total yield of phenanthrene derivatives is good.

The synthesis of 2-biphenylacetic acid by von Braun and Manz[5] has been accomplished by the

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[1] Bougault, *Comp. rend.*, **159**, 745 (1915); v. Auwers and Möller, *J. prakt. Chem.*, **109**, 124 (1925); Bardhan, *Nature*, **134**, 217 (1934); Fieser and Hershberg, THIS JOURNAL, **57**, 1508 (1935).

[2] Jeanes and Adams, THIS JOURNAL, **59**, 2608 (1937).

[3] Weizmann, Bergmann and Berlin, THIS JOURNAL, **60**, 1331 (1938).

[4] The synthesis of Weizmann, *et al.*[3] is based upon the preparation by Gruber and Adams [THIS JOURNAL, **57**, 2555 (1935)] of the adduct of dicyclohexenyl and maleic anhydride.

[5] Von Braun and Manz, *Ann.*, **468**, 273 (1929).