Acknowledgment.—We thank the National Research Council of Canada for financial assistance in this work. Our thanks are extended to Mrs. D. Mahlow of this department for the elemental analyses, to Mr. R. Swindlehurst and associates in this department for the 60-MHz spectra, to Mr. Swindlehurst for the infrared spectra, and to Mr. G. Bigham and associates of this department for the decoupling experiments and the 100-MHz spectra.

The Reaction of *p*-Chlorobenzotrifluoride with Methylsulfinyl Carbanion

JOSEPH A. MESCHINO* AND JAMES N. PLAMPIN

Department of Chemical Research, McNeil Laboratories, Inc., Fort Washington, Pennsylvania 19034

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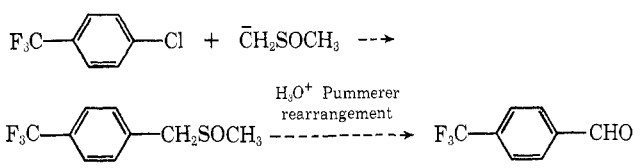
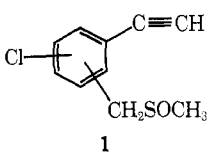
The preparation of *p*-trifluoromethylbenzaldehyde by the Grignard reaction using *p*-bromobenzotrifluoride and dimethylformamide has been reported.[1,2] The method suffers from the fact that the starting bromo compound is very expensive. Attempts here and elsewhere[1] to use the relatively inexpensive chloride have resulted in the isolation of only miniscular yields of *p*-trifluoromethylbenzaldehyde.[3] A search for an alternate method for its synthesis was therefore undertaken.

One approach was suggested by the report by Corey and Chaykovsky[4] that chlorobenzene reacts with methylsulfinyl carbanion to give methylbenzyl sulfoxide. Accordingly, the following sequence was investigated.



Treatment of *p*-chlorobenzotrifluoride with sodium methyl sulfinyl carbanion gave a dark, foul-smelling, oily product from which a solid slowly crystallized. Infrared and nmr analyses of the purified solid indicated the presence of a benzyl methyl sulfoxide part structure, but both spectra also indicated the presence of a monosubstituted acetylene. Elemental analysis gave empirical formula $C_{10}H_9ClOS$. These data strongly pointed to a structure such as **1**.



1

Several attempts to convert the substance to one more easily characterizable, *e.g.*, by reduction of the acetylene group and/or acid-catalyzed rearrangement of the sulfoxide group, were unsuccessful.

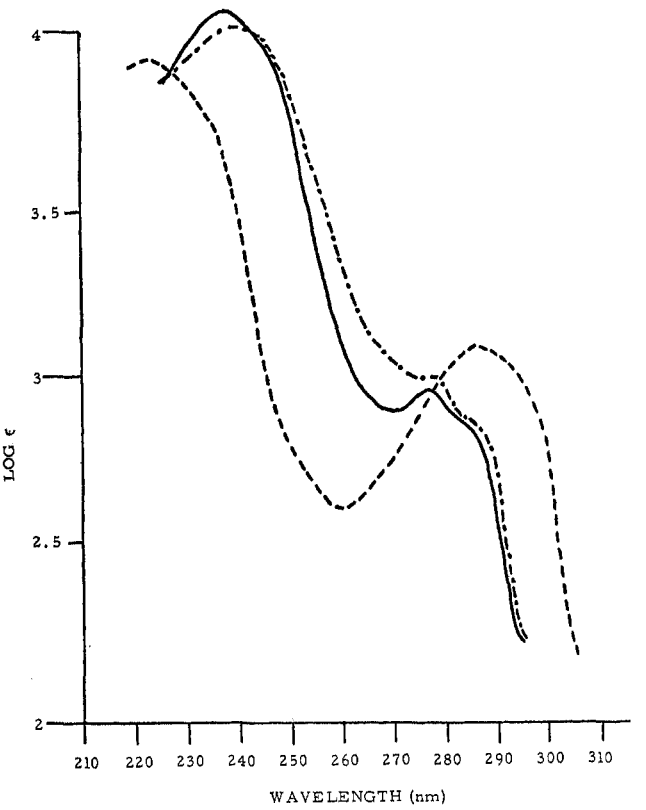
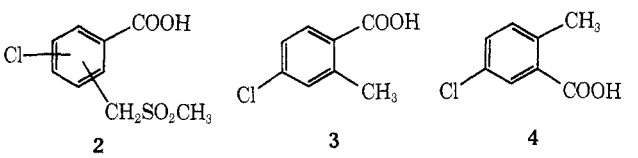


Figure 1.—Ultraviolet spectra: oxidation product (-·-·-); 5-Chloro-*o*-toluic acid (- - -); 4-chloro-*o*-toluic acid (——).

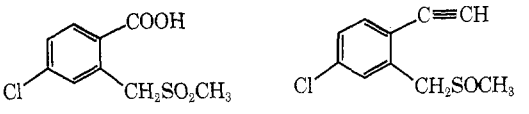
Ultraviolet spectral comparison to *m*- and *p*-chlorophenylacetylenes[5] was inconclusive (λ_{max}^{MeOH} 237, 248, 255 nm for the unknown; λ_{max}^{MeOH} 243, 248, 253 nm for *p*-chlorophenylacetylene; *m*-Chlorophenylacetylene shows λ_{max}^{MeOH} 237, 241, 247 nm).

Finally, oxidation with potassium permanganate gave a carboxylic acid sulfone **2** whose ultraviolet and nmr spectra were then compared to those of 4-chloro-*o*-toluic acid (**3**) and 5-chloro-*o*-toluic acid (**4**).[6]



2 **3** **4**

The ultraviolet and nmr comparisons are shown in Figures 1 and 2, respectively. The excellent correlation between the oxidation product and 4-chloro-*o*-toluic acid (3) leaves little doubt that the structure of the former is correctly shown as **5**, *i.e.*, 2-methylsulfonylmethyl-4-chlorobenzoic acid. The crystalline



5 **6**

(1) H. E. Ramsden, *et al.*, *J. Org. Chem.*, **22**, 1202 (1957).
(2) R. Filler and H. Novar, *ibid.*, **25**, 733 (1960).
(3) G. F. Holland, *et al.*, *J. Med. Chem.*, **6**, 519 (1963), report the use of *p*-chlorobenzotrifluoride to prepare this aldehyde. Unfortunately, no details are given.
(4) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1345 (1965).
(5) These were prepared from the corresponding acetophenones by the method of C. Dufraisse and A. Desquesnes, *Bull. Soc. Chim. Fr.*, **49**, 1880 (1931). See also, M. M. Otto, *J. Amer. Chem. Soc.*, **56**, 1393 (1934).
(6) We thank K & K Laboratories of Plainview, N. Y., for samples of these compounds which were unambiguously prepared from 4-chloro-2-methylaniline and 5-chloro-2-methylaniline, respectively.

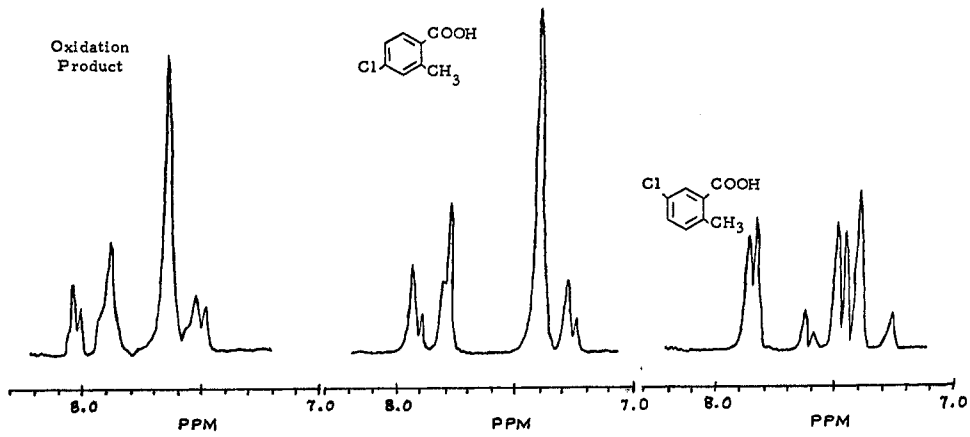
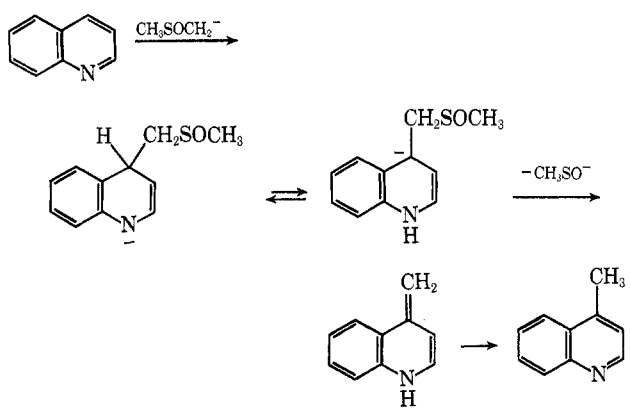


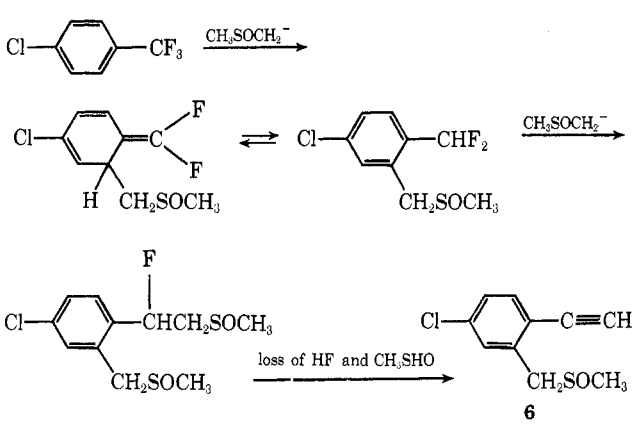
Figure 2.—Nmr spectra: oxidation product; 4-chloro-*o*-toluic acid; 5-chloro-*o*-toluic acid.

product isolated from the reaction of methylsulfinyl carbanion with *p*-chlorobenzotrifluoride is, therefore, **6**, *i.e.*, 5-chloro-2-ethynylbenzyl methyl sulfoxide.

Methylsulfinyl carbanion is known to add to some aromatic systems to give methylated products.[7] For example, the reaction sequence with quinoline to give 4-methylquinoline was pictured as follows.



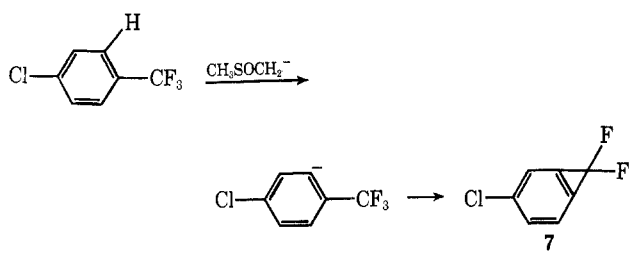
With *p*-chlorobenzotrifluoride, the sequence of events might be as follows.



6

Corey and Chaykovsky[4] have suggested the possibility of a benzyne intermediate in the transformation of chlorobenzene to methyl benzyl sulfoxide, and the involvement of an analogous species, such as **7**, is also a possibility in the present work.

(7) See, *e.g.*, G. A. Russell and S. A. Weiner, *J. Org. Chem.*, **31**, 248 (1966), and references cited therein.



7

Further clarification of the mechanism of this reaction is the subject of further investigation.

Experimental Section[8]

5-Chloro-2-ethynylbenzyl Methyl Sulfoxide (6).—A mixture of 28.8 g (1.2 mol) of sodium hydride, freed from oil by washing with petroleum ether, and 156 g (2 mol) of distilled, water-free dimethyl sulfoxide in 350 ml of THF was stirred and refluxed until hydrogen gas evolution ceased (about 2.5 hr). The mixture was cooled to −5°, under nitrogen, in an ice bath and treated dropwise with 36 g (0.2 mol) of *p*-chlorobenzotrifluoride in 25 ml of THF.[9] The temperature was kept at below 8° during the addition.

After stirring for about 2 hr, the bath was removed and the temperature allowed to reach room temperature. The reaction mixture was poured into a mixture of ice and water and extracted with benzene. The extracts were dried and treated with charcoal, and the solvent was distilled *in vacuo*, leaving a dark oily residue which deposited a solid on trituration with ether. The solid was collected (9 g) and recrystallized from ethyl acetate–hexane to give 5.1 g (12%) of **6**, mp 104–108°. Recrystallization from ethyl acetate–hexane gave 5 g of material: mp 112–114°; ir (KBr) 3200 (C≡CH), 2100 cm^{-1} (C≡CH); uv (MeOH) 237 nm (ε 14,900), 248 (15,620), 255 (14,550); nmr ($CDCl_3$) δ *ca.* 7.4 (m, 3, aromatic), 4.19 (s, 2, CH_2SO), 3.47 (s, 1, C≡CH), 2.52 ppm (s, 3, $SOCH_3$).

Anal. Calcd for $C_{10}H_9ClOS$: C, 56.47; H, 4.26; Cl, 16.67; S, 15.08. Found: C, 56.35; H, 4.30; Cl, 16.63; S, 15.20.

2-Methylsulfonylmethyl-4-chlorobenzoic Acid (5).—To a suspension of 1.1 g (0.005 mol) of 5-chloro-2-ethynylbenzyl methyl sulfoxide in 30 ml of water was added, with swirling and heating on a steam bath, 3.2 g (0.02 mol) of $KMnO_4$ in several portions. After a few minutes, the mixture was cooled, filtered through Celite, and acidified. The resulting precipitate was collected and washed with water to give 0.5 g (38%) of **5**: mp 193–196° (recrystallization from absolute ethanol raised the melting point 201–203°); ir (KBr) 1666 cm^{-1} (C=O); uv max (MeOH) 236

(8) All melting points are uncorrected and were taken on a Thomas-Hoover capillary melting point apparatus. The nmr spectra were taken on a Varian A-60 spectrometer with tetramethylsilane as internal standard. The elemental analyses were performed by Scandinavian Microanalytical Laboratories, Herlev, Denmark.

(9) *Caution:* The reaction is very exothermic, and, if the addition is not carried out slowly, a violent eruption may occur.

nm (ε 9660), 279 (960), 286 (745); nmr (DMSO-d_6) δ *ca.* 7.8 (m, 3, aromatic), 5.07 (s, 2, CH_2SO_2), 2.91 ppm (s, 3, SO_2CH_3).

Anal. Calcd for $C_9H_9ClO_4S$: C, 43.46; H, 3.65; Cl, 14.26; 14.26; S, 12.90. Found: C, 43.47; H, 3.65; Cl, 14.45; S, 12.76.

Registry No.—**3**, 7499-07-2; **4**, 7499-06-1; **5**, 31579-08-5; **6**, 31579-09-6; *p*-chlorobenzotrifluoride, 98-56-6; methylsulfinyl carbanion, 13810-16-7.

Acknowledgment.—We wish to thank Dr. Harold R. Almond for the spectroscopic data and his assistance in their interpretation.

An Investigation of the Formation of By-Products in the Nitration of Pentachlorobenzene

T. G. JACKSON,* J. E. NORRIS, AND R. C. LEGENDRE

Department of Chemistry, University of South Alabama, Mobile, Alabama 36608

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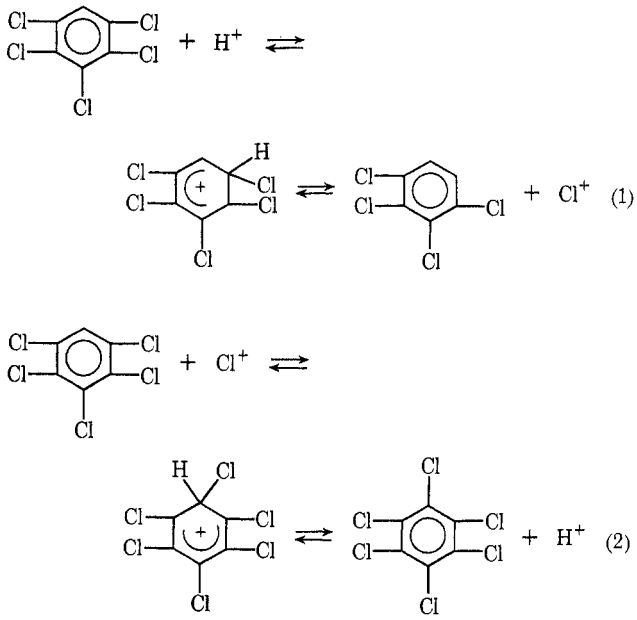
Pentachloronitrobenzene (PCNB) is an extensively used soil fungicide produced by both foreign and domestic manufacturers. A variety of methods have been used in the production of PCNB,[1-3] but it is commonly prepared by the direct nitration of pentachlorobenzene (PCB).

We have observed in our investigation of this process that the desired PCNB is produced in 83–89% yield based on the amount of PCB reacting, some unchanged PCB being recovered due to sublimation thus removing it from the nitrating mixture. Careful analysis of the reaction mixture by gas chromatography showed that a by-product, hexachlorobenzene (HCB), is formed during the course of reaction.

It was first suspected that the possible displacement of a chloronium ion from the PCB by a proton from the acids employed, with subsequent attack of this chloronium ion on PCB, would lead ultimately to formation of HCB. This mechanism may be represented by eq 1 and 2. This route was discarded as a likely mechanism when only two products, HCB and PCNB, were found in the reaction mixture; no detectable amount of tetrachlorobenzene was produced in the nitration of PCB. In addition, no hexachlorobenzene or tetrachlorobenzene could be detected when PCB was heated with fuming sulfuric acid, even for extended periods of time.

In subsequent studies of the nitration of PCB, the presence of molecular chlorine as a reaction product was established. It has then been postulated that the molecular chlorine arose *via* destructive oxidation of PCB since it is known that ring oxidation is sometimes a significant side reaction in the direct nitration of aromatic systems.[4] The destructive oxidation process



of PCB would be expected to give, in addition to molecular chlorine, low-molecular-weight fragments. Infrared and nmr analysis of the off-gas from the nitration process established the presence of the products identified generally as low-molecular-weight carboxylic acids. No aromatic products were observed in the off-gas. Subsequent attack of the molecular chlorine on PCB would lead to the formation of the observed HCB. The process involves chlorination of the aromatic system in the absence of catalyst (ZnX_2, FeX_3, etc.) normally employed in halogenations. The reaction path followed is probably similar to that suggested in earlier halogenation studies by Keefer and Andrews.[5,6] The molecular chlorine reacts with the PCB to form an aromatic halogen π complex, which collapses into a σ complex as a result of attack on the halogen–halogen bond by a polar reagent. It has been suggested[5] that in the absence of a catalyst the halogen itself may fill the role of the polar reagent. However, under the conditions of the nitration of PCB, there are a number of species formed that are stronger electrophilic reagents than chlorine and are more likely to function as the polar reagent.

It has also been observed that HCB is formed in small amounts when PCB is heated with fuming nitric acid, the amount of HCB formed in a given time being increased by the introduction of anhydrous chlorine. Treatment of PCB with anhydrous chlorine in the presence of hydrochloric acid or anhydrous hydrogen chloride gave no detectable amount of HCB in reaction periods up to 1.5 hr. This lends support to the concept that chlorination of PCB to form HCB is promoted by some polar reagent formed during the nitration process or by nitric acid itself.

Experimental Section

Gas chromatographic analyses were performed on a Hewlett-Packard F & M Model 700 chromatograph. Columns used in this study were 10% OV-17 silicone on Chromosorb G, H. P., 80–100 mesh, 5% Carbowax 20M on Anakrom AS, 80–90 mesh, and 5% Aroclor 1232 on Chromosorb T, 40–60 mesh. Ir spectra

(1) H. Furst, H. Dietz, P. Ehrentrant, and P. Rammelt, German (East) Patent 10,655 (Oct. 19, 1955); *Chem. Abstr.*, **52**, P-16288e (1956).

(2) E. A. Lojewski, U. S. Patent 30,26358 (March 20, 1962); *Chem. Abstr.*, **57**, 7170*f* (1962).

(3) M. Hedayatullah, C. Olle, and L. Dienville, *C. R. Acad. Sci., Ser. C*, **264**, 106 (1967); *Chem. Abstr.*, **66**, 104756e (1968).

(4) J. Hine, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1956, p 332.

(5) R. M. Keefer and L. J. Andrews, *J. Amer. Chem. Soc.*, **78**, 5626 (1956).

(6) L. J. Andrews and R. M. Keefer, *ibid.*, **79**, 5172 (1957).