The plane of the heterocycle (approximately coincident with the crystallographic glide plane) is nearly a mirror plane of each of the four rings. However, this molecular symmetry is violated by the essentially flat carbomethoxyl groups which are rotated unsymmetrically about the C-C bonds through various angles (in the pyrrolinyl ring, 87, 2°; adjacent in the cyclopentadienyl ring, 25, 40, 55, 4°) in order to relieve nonbonded steric interactions. The equal geminal C—N bond lengths (1.33 Å) and the coplanarity of all atoms bonded to the two nitrogen atoms suggest a delocalized amidine structure. Both cyclohexyl rings appear oriented so as to allow close approach of the protonated amidine to the bromide ion. The latter ion also lies essentially in the heterocyclic plane within hydrogen bonding distance (3.32 Å) of the exocyclic nitrogen atom which presumably bears the proton. The other Br^----N distance is 4.46 Å.

The structure of this 3:2 adduct can be formally derived by the addition of the dipolar 1:1 adduct **3** to the C=N bond of the 2:1 adduct **4**. However, in the absence of further chemical information, we cannot comment on the structure of its isomeric precursor **6**.

Registry No.—**1,** 762-42-5; 2 (R′ = C_6H_{11}), 931-53-3; **7,** 31528-92-4; **7** HBr, 31528-93-5.

Configuration and Conformation of the Dibromides Obtained from the Reaction of Bromine with 2-Ethoxy-5,6-dihydro-2*H*-pyran[1]

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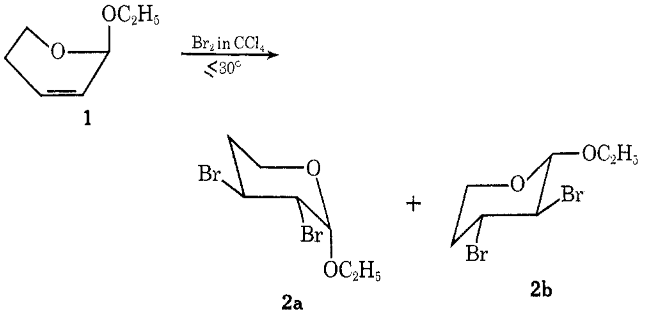
Received January 25, 1971

It has been reported[5] that the reaction of bromine with 2-ethoxy-5,6-dihydro-2*H*-pyran (**1**) produces a mixture of "two geometrical isomers of 2-ethoxy-3,4-dibromotetrahydropyran" (Scheme I). Although the separation of these isomers has been described,[5] no conformational assignment was made apart from the assumption that the two vicinal bromine atoms were mutually trans.[5] Our program of study of 2-alkoxydihydro- and tetrahydropyrans required a knowledge of the configurational and conformational details of these dibromides in order to determine their influence on the relative stability of the α and β anomers (the anomeric effect[6-8]) and on the course of the base-catalyzed dehydrohalogenation of the dibromides. This note reports our findings concerning the configuration and conformation of these dibromides.

SCHEME I



Low-temperature (≤30°) bromination of **1** either in carbon tetrachloride or methylene chloride gave a mixture of dibromides in 71% yield (*cf.* 68%[5]). Bromination in methylene chloride at −80° or −40 to −45° provided a mixture in which the two isomers **2a** and **2b** were present in the approximate ratio 3:1, determined by the proton magnetic resonance (pmr) spectrum of the isolated crude mixture. An increase in reaction temperature to −30° changed the proportion to ~2:1. Bromination in carbon tetrachloride at either −45 or −30° gave **2a** and **2b** in the ratio ~2:1.

The minor constituent, **2b**, a solid, was separated in the pure state from the liquid mixture by crystallization as reported previously.[5] This did not give quantitative separation. However, most of the remainder of **2b** could be obtained from the residue left when the mother liquor was distilled. The major component, **2a**, a liquid obtained by vacuum fractional distillation of the mother liquor, was found to be contaminated by a small amount (<5%) of **2b** which extensive and careful fractional distillation failed to remove. However, subsequent gas–liquid chromatography (glc) of this distilled fraction did provide pure **2a**. Elemental analyses of the individual isomers agreed with that required for a dibromo-2-ethoxytetrahydropyran.

The configuration and conformation of the solid isomer **2b** was examined by pmr. The 100-MHz spectrum obtained in deuteriochloroform and referred to tetramethylsilane showed the anomeric proton signal as a doublet centered at τ 5.52 ($J_{2,3}$ ~ 7.0 Hz). In either acetonitrile or acetonitrile saturated with tetra-*n*-butylammonium bromide, the anomeric proton signal was found at τ 5.54 with $J_{2,3}$ ~ 7.8 Hz. The large coupling, as well as the change observed when acetonitrile was used as solvent, shows that the C-2 ethoxy group and the C-3 bromine atom are trans and equatorial.[9] By irradiation at appropriate frequencies, in spin decoupling experiments, it was possible to locate the signals for both H-3 and H-4. A first-order analysis showed a large coupling, $J_{3,4}$ ~ 9.8 Hz, indicating that these two protons are trans diaxially disposed and therefore that the two bromine atoms attached to C-3 and C-4 are trans and equatorial. The above information clearly shows that the solid isomer has the configuration shown by **2b** and that the preferred conformation of **2b** is that in which all the substituents are equatorial.

The 100-MHz pmr spectrum of the liquid isomer, **2a**, in deuteriochloroform possessed a doublet for the anomeric proton signal at τ 5.12 ($J_{2,3}$ ~ 2.8 Hz) which is nearly the same as that obtained in acetonitrile or ace-

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[1] In part from the thesis of F. Sweet, presented to the Faculty of Graduate Studies, University of Alberta, Edmonton, Alberta, Canada, in partial fulfillment of the requirements for the Ph.D. degree.

[2] Postdoctoral Fellow, 1968–1970.

[3] Postdoctoral Fellow, 1969–1971.

[4] Author to whom correspondence should be directed.

[5] G. F. Woods and S. C. Temin, *J. Amer. Chem. Soc.*, **72**, 139 (1950).

[6] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Wiley, New York, N. Y., 1965, pp 375–377.

[7] C. B. Anderson and D. T. Sepp, *Chem. Ind. (London)*, 2054 (1964).

[8] E. L. Eliel and C. A. Giza, *J. Org. Chem.*, **33**, 3754 (1968).

[9] R. U. Lemieux, R. K. Kullnig, H. J. Bernstein, and W. G. Schneider, *J. Amer. Chem. Soc.*, **80**, 6098 (1958).

tonitrile saturated with tetra-*n*-butylammonium bromide (τ 5.10, $J_{2,3} \sim 2.8$ Hz). By irradiation of the H-2 nucelus at τ 5.12, the quartet centered at τ 5.89 collapsed to a doublet ($J_{3,4} \sim 10$ Hz), showing that the quartet at τ 5.89 was due to H-3. The large coupling (10 Hz) between H-3 and H-4 proved that these two protons are trans and diaxial and therefore the two bromine atoms are trans and diequatorial. The value of 2.8 Hz for $J_{2,3}$ establishes that the protons on C-2 and C-3 are either gauche (equatorial–axial) or trans diequatorial. Since it has been shown that the C-2 ethoxy group in **2b** is equatorial, and that **2a** and **2b** are isomeric, both having substituents only on C-2, C-3, and C-4, it follows that **2a** differs from **2b** in the configuration at C-2. Accordingly, the ethoxy group at C-2 in **2a** must be axial and thus the configuration and preferred conformation of the liquid isomer is that shown by **2a** in Scheme I.

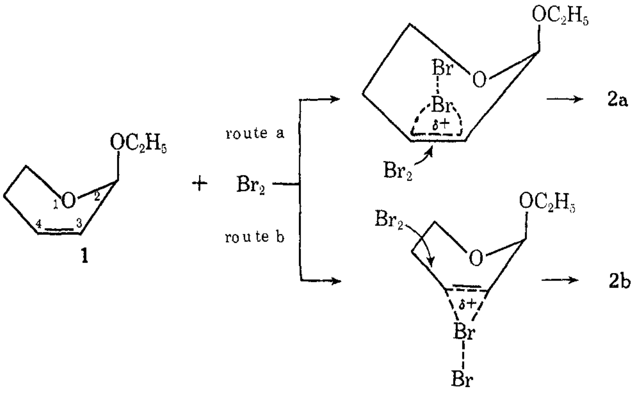
Further support for the structure and conformation of the two isomeric dibromides as shown by **2a** and **2b** in Scheme I is provided by the relative pmr chemical shifts of the signals for the anomeric protons. It is known that an anomeric proton in the axial position provides a signal in the nmr spectrum at higher field than does the anomeric proton in an equatorial orientation.[9] In accord with this is the signal position of the anomeric proton of **2b** at τ 5.52 while that of **2a** is at τ 5.10. Strong bands at 730 and 740 cm^{-1} in the infrared spectra of **2a** and **2b**, respectively, also are indicative of equatorial C–Br stretching. No absorption was found in the region of 550 cm^{-1}, characteristic of axial C–Br.

Whether the proportion of the two isomers obtained is a result of direct bromination of **1**, or of the preferential formation of one isomer which isomerizes in part to the other isomer, is not clear. The same proportion of the two isomers was obtained either when the mixture was worked up immediately following complete addition of the bromine, or when the mixture was allowed to stand for 60 hr after the bromine addition and then worked up. Attempts at isomerization or equilibration by heating either **2a** or **2b** from 12 to 14 hr in refluxing absolute ethanol containing *p*-toluenesulfonic acid gave no appreciable change in either isomer. The marked stability of these dibromides to hydrolysis has already been noted.[5] However, when a methylene chloride solution of pure **2b** at $-30°$ was treated for 0.5 hr with dry hydrogen bromide gas, and the resulting solution was first allowed to stand for an additional 2.5 hr at $-30°$, then come to room temperature over a 4-hr period, and finally kept in a refrigerator overnight, a crude material was obtained whose 100-MHz pmr spectrum showed **2a** and **2b** to be present in the ratio 1.5:1.0, respectively. Similar treatment of **2a** containing 14% of **2b** as contaminant (**2a**:**2b** $\approx$ 6:1) gave a crude product containing **2a** and **2b** in the proportions of $\sim$10:1. Under these conditions, **2b** is converted to **2a** but the reverse conversion appears to be much more difficult. It is significant that, in both cases involving treatment of **2a** or **2b** with dry hydrogen bromide in methylene chloride, the pmr spectrum of the crude product contained signals (unidentified) not found in the pmr spectrum of the crude product of bromination of **1**. This indicates that the normal conditions of bromination of **1** are not so severe as those involving isomerization of **2a** or **2b** with hydrogen bromide.

To determine whether isomerization of **2b** to **2a** might have been caused by hydrogen bromide present in the bromine, or by the hydrogen bromide produced by a side reaction such as substitution, 0.1 molar equiv of bromine was added over a 1-hr period to a solution of **2b** in methylene chloride kept at $-30°$, and the mixture was then allowed to approach room temperature for 1 hr. During this time all the color of bromine slowly disappeared. The pmr spectrum of the isolated crude material showed no evidence whatsoever of the formation of **2a**.

The evidence above in our view indicates that the proportion of isomers **2a** and **2b** does arise from a direct bromination process. Bearing on this problem is our finding[10] that the double bond of 2-methoxy-5,6-dihydro-2*H*-pyran, the methyl homolog of **1**, is attacked by osmic acid apparently only from the side trans to the C-2 methoxy group, thus indicating that this dihydropyran strongly prefers to react in the conformation in which the methoxy group at C-2 is pseudoaxial. If this is so, then compound **1** (Scheme I) should prefer a similar conformation. Pertinent to this is the report[11] that the 2-alkoxy group in both *cis*- and *trans*-2-alkoxy-5,6-dihydro-2*H*-pyran-6-carboxylic esters prefers the pseudoaxial conformation. As well, we have shown[12] that 2-methoxy-5,6-dihydro-2*H*-pyran in ether–methanol reacts with 1,3-dibromo-5,5-dimethylhydantoin to give the two isomers 3β-bromo-2α,4α-dimethoxytetrahydropyran and 3α-bromo-2α,4β-dimethoxytetrahydropyran, thus showing that the bromine atom invariably ends up on C-3, the carbon atom of the double bond closer to the anomeric center C-2, while the methoxy group is attached to C-4 (Scheme II in ref 12). If a bromonium ion is involved in this latter reaction as has been suggested,[12] and this occurs also in the reaction of bromine with **1**, and taking into account our findings,[12] it is clear that **2a** could be formed by route a shown in Scheme II, while **2b** could then be formed by the alternate route (b) in Scheme II. In each case, the bromine atom of the bromonium ion becomes attached to C-3. The greater proportion of **2a** must then mean that bromine prefers to attack the double bond from the side cis to the C-2 ethoxy group in spite of the apparent

Scheme II



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[10] R. M. Srivastava and R. K. Brown, *Can. J. Chem.*, **49**, 1339 (1971).

[11] O. Achmatowicz, Jr., J. Jurczak, A. Konowal, and A. Zamojski, *Org. Magn. Resonance*, **2**, 55 (1970).

[12] M. J. Baldwin and R. K. Brown, *Can. J. Chem.*, **47**, 3099 (1969).

steric opposition[10] due to this substituent. It is conceivable that an association occurs between the bromine molecule and the electron pairs of the ethoxy group and this causes the predominance in attack by bromine on the double bond on the same side of the ring as is occupied by the ethoxy group.

Experimental Section

All melting points and boiling points are uncorrected. The micro boiling point was determined by using a two-bulb microdistillation apparatus whose lower bulb was immersed in an oil bath. The bath was heated slowly, and, when the liquid started to boil, the temperature of the bath was recorded as the boiling point. Gas–liquid chromatography (glpc) analyses were made with an F & M Model 700 instrument using 0.125 × 12 in. columns. For isolation purposes, an Aerograph Autoprep Model A-700 was employed. Helium was the carrier gas. Solvents were removed by rotary evaporator under vacuum unless otherwise stated. The 60-MHz pmr spectra were obtained with a Varian 60-MHz spectrometer. The 100-MHz spectra and decoupling experiments were made with a Varian HR 100-MHz spectrometer. Tetramethylsilane was the reference material. The infrared spectra were obtained with a Perkin-Elmer Model 421 grating spectrometer.

***trans*-3-Bromo-2-ethoxytetrahydropyran** was prepared by the same method used to make *trans*-3-bromo-2-methoxytetrahydropyran[13] but using absolute ethanol rather than methanol as solvent. From 84 g (1.0 mol) of 3,4-dihydro-2*H*-pyran there was obtained 85 g (41%) of crude 3-bromo-2-ethoxytetrahydropyran. This was distilled and the fraction (60 g) boiling at 64–66° (2.8 mm) was collected, n^{21}D 1.4760 [lit.[14] bp 94–96° (18 mm); n^{25}D 1.4752 for material made by the reaction of 2,3-dibromotetrahydropyran with dry ethanol and ammonia].

Both the pmr ($CDCl_3$) and the glc spectra showed our material to be a mixture of cis and trans isomers in the ratio of 1:4, respectively.

Preparation of 3-bromo-2-ethoxytetrahydropyran by the method of Woods and Sanders[14] gave a cis–trans ratio of 2:1.

3,4-Dibromo-2-ethoxytetrahydropyran (2).—This compound was prepared by the following modification of the published procedure.[5]

The bromination was carried out in carbon tetrachloride at −45 to −40° rather than at −30°. When all the bromine had been added, the reaction flask was removed from the cooling bath and the solution was stirred for 1 hr, during which time the mixture came to room temperature. The mixture was washed six times with an aqueous solution of a mixture of sodium sulfite (~15%) and sodium carbonate (~15%) and then thrice with water. The last water wash still showed a faint acidic reaction to litmus. The organic solution was dried (Na_2SO_4) and then freed from the drying agent and solvent. The pmr spectrum of the crude residue in $CDCl_3$ showed that it was nearly all a 2:1 mixture of **2a** and **2b**. The weight of this crude material indicated that the bromination had occurred nearly quantitatively.

To avoid extensive decomposition during the subsequent distillation step due to residual acid, the crude material was dissolved in ether and the solution was washed six times with aqueous sodium carbonate (~30%) and then thoroughly with water. The ether solution was dried over a mixture of anhydrous sodium sulfate and sodium carbonate. Removal of the drying agent and solvent gave a colorless liquid (83% crude yield) which was distilled and the fraction collected which boiled at 77–81° (0.2–0.5 mm), yield 71%. At room temperature, this slowly turned yellow. The infrared spectrum (neat) showed two very weak bands at 1700 and 1615 cm^{-1} indicative of a trace of contamination (<1%) by a substance containing a carbonyl group. This impurity was then removed by washing a carbon tetrachloride solution of the oil, first with aqueous sodium carbonate (25%), then with aqueous sodium bisulfate (25%), and finally with water. The oil then isolated could be distilled without decomposition, yielding a stable, pure substance.

Separation of the solid isomer, **2b**, was accomplished by precipitation from cold pentane.[5] The recrystallized material (from pentane) melted at 58–58.5° (lit.[5] mp 60–61°).

The ir spectrum (Nujol mull) showed a strong, sharp band at 740 cm^{-1} (equatorial C–Br); 100-MHz pmr ($CDCl_3$) τ 5.52 (d, 1, J = 7.0 Hz, HC_2O), 5.94 (sextet, J = 9.8 and 5.0 Hz, HC_4Br), 6.10 (q, 1, J = 9.8 and 7.0 Hz, HC_3Br), 6.45 (m, 4, $-CH_2O$, $-C_6H_2O$), 7.75 (m, 2, $-C_5H_2-$), 8.74 (t, 3, J = 7.0 Hz, $-CH_3$).

The mother liquid was distilled with a spinning-band column and provided **2a**, bp 74° (0.5 mm), contaminated with **2b** (<5% by 100-MHz pmr). Glc on a column of 20% butanediol succinate on Gas-Chrom P (60–80 mesh) at 170° with a helium gas flow rate of 80 ml/min showed two peaks, one of which was minute, but the isolated major component **2a** invariably contained decomposition products. Glc on a 0.25 in. × 5 ft column of 20% diethylene glycol succinate on Gas-Chrom W (60–80 mesh) with column and injection port temperatures at 145 and 180°, respectively, and helium carrier gas flow at 100 ml/min and with 10-μl quantities at each injection gave satisfactory isolation of pure **2a** (major peak), bp 74–74.5° (0.5 mm), by two-bulb microdistillation, n^{23}D 1.5155 [lit.[5] bp 123° (12 mm); n^{25}D 1.5158].

Anal. Calcd for $C_7H_{12}O_2Br_2$: C, 29.19; H, 4.20; Br, 55.50. Found: C, 29.48; H, 4.37; Br, 55.42.

The ir spectrum (neat) showed a strong, sharp band at 730 cm^{-1} (equatorial C–Br); 100-MHz pmr ($CDCl_3$) τ 5.12 (d, 1, J = 2.8 Hz, HC_2O), 5.50 (sextet, 1, J = 10.0 and 4.8 Hz, HC_4Br), 5.89 (q, 1, J = 10.0 and 2.8 Hz, HC_3Br), 6.32 (m, 4, $-CH_2O$, $-C_6H_2O$), 7.70 (m, 2, $-C_5H_2-$), 8.74 (t, 3, J = 7.0 Hz, $-CH_3$).

When the bromination was carried out at −30° in carbon tetrachloride, the proportion of **2a** to **2b** in the crude product was found by its pmr spectrum to be ~2:1. Bromination in methylene chloride at −45 to −40° gave **2a**:**2b** ≈ 3:1 whereas bromination in this solvent at −30° gave **2a**:**2b** ≈ 2:1.

Attempted Isomerization of 2a and 2b. A. In Acidified Ethanol.—A solution of 250 mg of the liquid isomer **2a** in 10 ml of absolute ethanol containing 100 mg of *p*-toluenesulfonic acid monohydrate was heated under reflux for 24 hr. The solution was cooled and made alkaline with 10% ethanolic potassium hydride (5 ml). The solvent was removed and the residue was treated with 50 ml of diethyl ether. The precipitated salt was removed and the filtrate was washed with water (three 5-ml portions) and dried (Na_2SO_4). Removal of the drying agent and solvent afforded 200 mg of **2a**. The pmr spectrum in $CDCl_3$ gave no indication of the presence of **2b**.

Similarly, **2b** was heated under reflux for 12 hr and the product was worked up as above. The pmr spectrum of the isolated material showed no evidence of the presence of **2a**. The spectrum did show a new broadened singlet at τ 5.14, but this was not due to **2a**, since the anomeric proton of **2a** produces a doublet at τ 5.10. This contamination was of the order of 10–15%.

B. In Methylene Chloride in the Presence of Hydrogen Bromide.—A solution of 400 mg of pure **2b** in 10 ml of dry methylene chloride was cooled to −30° in a Dry Ice–acetone bath. Dry hydrogen bromide gas was passed through the solution for 5 min. The mixture then was stirred and kept at −30° for 2.5 hr and then the cooling bath was removed and the stirred solution allowed to come to room temperature over a period of 4 hr. After being kept in the refrigerator overnight, during which time it became yellow, the solution was diluted with 10 ml of methylene chloride, then washed with 10% aqueous sodium carbonate (three 10-ml portions) and finally with water (four 10-ml portions). The organic layer was dried (Na_2SO_4) and freed from drying agent and solvent and gave 280 mg of oil. The 60-MHz pmr spectrum showed a new doublet at τ 5.12 (J = 2.8 Hz) indicative of the anomeric proton of **2a**. Comparison of the integrated areas of the anomeric proton signals at τ 5.12 (for **2a**) and 5.52 (for **2b**) with that at τ 8.74 for the triplet for the protons of the methyl group shows that the proportion of **2a**:**2b** ≈ 1.5:1.0. In addition, two minor signals of unknown origin appeared at τ 4.57 (d, J ≈ 2.0 Hz) and 3.52 (d, J ≈ 2.8 Hz).

A solution of 400 mg of **2a** containing 14% of **2b** (**2a**:**2b** ≈ 6.16:1.0) in methylene chloride was treated as described above for pure **2b**. Light yellow liquid (337 mg) was obtained. The integrated areas of the anomeric proton signals showed the presence of **2a**:**2b** ≈ 10.1:1.0. New signals appeared at τ 3.53 (d, J = 3 Hz) and in the region τ 7.70.

Registry No.—**1**, 13687-95-1; **2a**, 31599-27-6; **2b**, 31599-28-7; bromine, 7726-95-6.

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[13] F. Sweet and R. K. Brown, *Can. J. Chem.*, **46**, 707 (1968).

[14] G. F. Woods and H. Sanders, *J. Amer. Chem. Soc.*, **68**, 2483 (1946).

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

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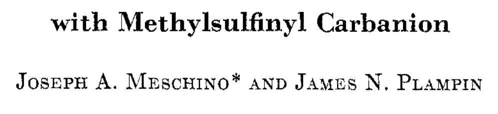
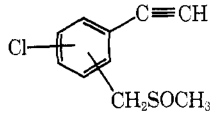
Received April 23, 1971

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**.



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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.

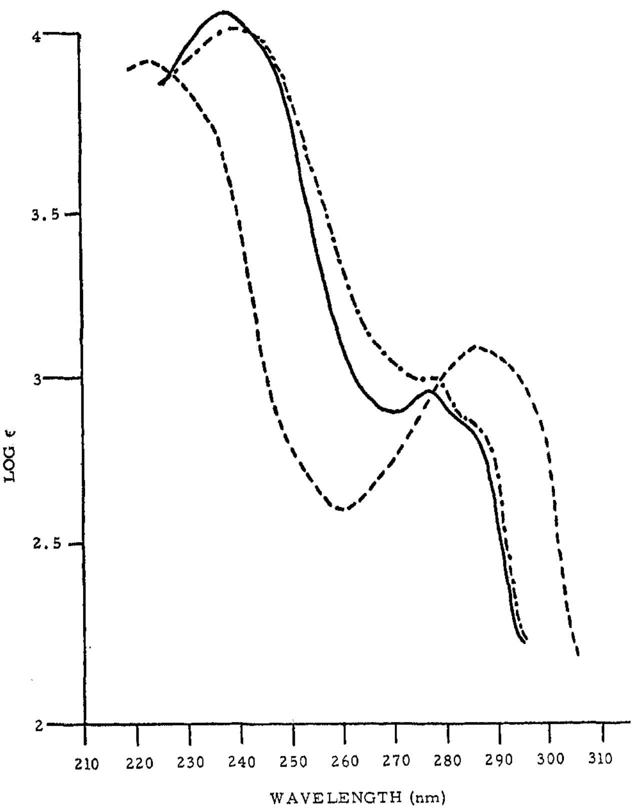
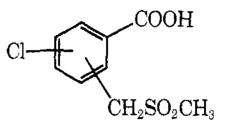


Figure 1.—Ultraviolet spectra: oxidation product (–·–·); 5-Chloro-*o*-toluic acid (– – –); 4-chloro-*o*-toluic acid (——).

Ultraviolet spectral comparison to *m*- and *p*-chlorophenylacetylenes[5] was inconclusive ($\lambda_{\max}^{\mathrm{MeOH}}$ 237, 248, 255 nm for the unknown; $\lambda_{\max}^{\mathrm{MeOH}}$ 243, 248, 253 nm for *p*-chlorophenylacetylene; *m*-Chlorophenylacetylene shows $\lambda_{\max}^{\mathrm{MeOH}}$ 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]



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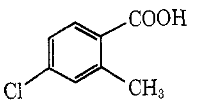

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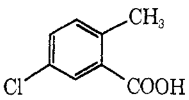

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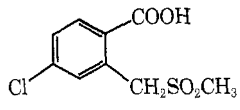
The ultraviolet and nmr comparisons are shown in Figures 1 and 2, respectively. The excellent correlation between the oxidation product and 4-chloro-*o*-toluic acid (**3**) leaves little doubt that the structure of the former is correctly shown as **5**, *i.e.*, 2-methylsulfonylmethyl-4-chlorobenzoic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



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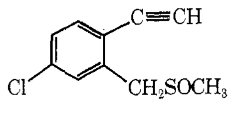

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[1] H. E. Ramsden, *et al.*, *J. Org. Chem.*, **22**, 1202 (1957).

[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.