

with the cooled material showed it to be completely soluble in alkali. The reaction product was treated with sodium carbonate solution, to remove unchanged crotonic acid, the residue was washed with water, and recrystallized from alcohol. When the crotonate was heated on the water-bath for fifteen minutes with 10% sodium hydroxide, and the solution acidified, XXXIV (m. p. 113°) separated.

1 - Phenyl - 1 - acetoxy - 2 - *p* - toluenesulfonamidoethane (XXXVIII).—A solution of 55 g. of IV in 100 cc. of glacial acetic acid was warmed on the water-bath until a test portion showed it to be completely soluble in alkali. This required thirty minutes. Too much heating renders the isolation of a crystalline acetate a difficult matter. The solution was poured in a fine stream into a liter of ice water. After standing for thirty minutes, the crystals were collected by filtration and air-dried. The yield was 65 g. (97% of the theoretical); m. p. 105°. The same acetate was obtained by refluxing for six hours 1 g. of XXIX (m. p. 111°) with 0.4 g. of anhydrous sodium acetate in 10 cc. of glacial acetic acid.

2-Phenyl-2-hydroxyethylamine.—A solution of 10 g. of XXXIV in 250 cc. of amyl alcohol was brought to boiling, and 18 g. of metallic sodium gradually added. The solu-

tion was then worked up in the usual manner. The amine was recovered in the form of a semi-solid mass, which when exposed to carbon dioxide yielded the known carbonate, m. p. 115°. The picrate melted at 158°.

Summary

1. Halosulfonamides of the type R'SO₂NBrR react with a large number of olefins to yield products in which the bromine atom takes the same position as the bromine atom in the "normal" addition of hydrogen bromide to these substances.

2. The N,N-dibromosulfonamides, on the other hand, add to olefins to give products in which the bromine atom takes the same position as the bromine atom in the "abnormal" addition of hydrogen bromide to these compounds.

3. The preparation of N-(*p*-tolylsulfonyl)-styreneimine and its reactions with various reagents are reported.

CHICAGO, ILLINOIS

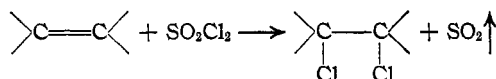
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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Chlorinations with Sulfuryl Chloride. II. The Peroxide-Catalyzed Reaction of Sulfuryl Chloride with Ethylenic Compounds

By M. S. KHARASCH AND HERBERT C. BROWN¹

Sulfuryl chloride reacts readily with most ethylenic compounds to yield the saturated dichloro derivatives and sulfur dioxide.

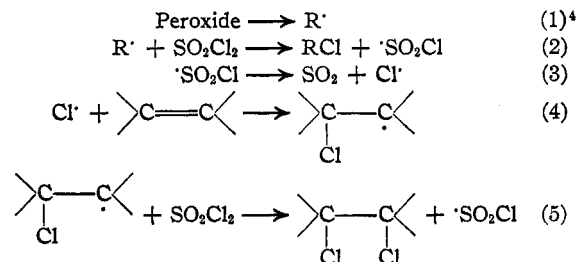


Although this reaction has been used for synthetic purposes,² no thorough study has been made of the factors which control these additions.

We have previously shown that the presence of small quantities of organic peroxides brings about a reaction between sulfuryl chloride and saturated aliphatic hydrocarbons.³ The characteristics of the reaction of sulfuryl chloride with olefins led us to suspect that this reaction is also peroxide-catalyzed. Investigation has confirmed this belief, and the evidence we have obtained indicates that the mechanism of this reaction is similar to

that involved in the peroxide-catalyzed reaction of sulfuryl chloride with aliphatic hydrocarbons, a chain reaction involving chlorine atoms.

The following mechanism is in full agreement with the experimental facts and is advanced as representing the most probable course of the reaction in the light of our present-day information.



That the reaction is peroxide-catalyzed is indicated by a number of observations. Thus, an old sample of cyclohexene (which gave a strong test for peroxides) reacted with sulfuryl chloride with explosive violence when the two substances were mixed at room temperature. When the

(1) Eli Lilly Fellow, 1938-1939.

(2) A search of the literature reveals the use of sulfuryl chloride for the chlorination of unsaturated substances in the following instances: (a) chlorination of tetraphenylethylene and its derivatives, Norris, Thomas and Brown, *Ber.*, **43**, 2949 (1910); (b) chlorination of cinnamic acid and cinnamyl aldehyde, Durrans, *J. Chem. Soc.*, **123**, 1424 (1923); (c) chlorination of cyclohexene, Frieze and Djiang, *Ber.*, **71**, 667 (1938); and (d) chlorination of 3-hexene, Spiegler and Tinker, *THIS JOURNAL*, **61**, 940 (1939).

(3) Kharasch and Brown, *ibid.*, **61**, 2142 (1939).

(4) The dot denotes an unshared electron. The evidence for the assumption that the catalytic effect of peroxides in these chlorinations is due to their decomposition into organic free radicals, is discussed in the first paper of this series: *ibid.*, **61**, 2149 (1939).

cyclohexene was distilled carefully immediately before use (weak peroxide test), a moderate reaction ensued only after an induction period of several minutes. Addition of a drop or two of old cyclohexene, benzaldehyde, or ascaridole to the freshly-distilled cyclohexene catalyzes the reaction and eliminates the initial induction period. Passage of dry air through the relatively inactive cyclohexene also enhances its reactivity. The reactivity of **allyl chloride** is similarly enhanced by peroxidic materials.

Unsaturated compounds which are less sensitive to traces of peroxide can be purified easily to such a degree that no appreciable reaction with sulfuryl chloride occurs in the absence of added peroxide. For example, pure *sym*-**dichloroethylene** can be heated with sulfuryl chloride under reflux for several hours without appreciable reaction. In the presence of a small quantity (0.002 mole) of benzoyl peroxide, however, reaction occurs smoothly to yield *sym*-tetrachloroethane. **Tetrachloroethylene** reacts in a similar manner to form hexachloroethane. This reaction is, however, very slow (15% in five hours) compared to the other olefin chlorinations studied.

Stilbene readily reacts to yield the two isomeric stilbene dichlorides, and **tetraphenylethylene** forms the corresponding dichloride. In previous work on the chlorination of tetraphenylethylene with sulfuryl chloride,^{2a} it was reported that different samples of sulfuryl chloride showed different capacities for reacting with tetraphenylethylene. The "inactive" samples could be activated by the addition of small quantities of acetic acid. We have repeated this work and have found that in the dark peroxide-free acetic acid does not catalyze the reaction of sulfuryl chloride, either with this olefin or with any of the others which we have tested (dichloroethylene, tetrachloroethylene, and stilbene). It appears likely that the activation was produced by the presence of peroxidic impurities in the acetic acid.

We have also carried out some preliminary studies of the action of sulfuryl chloride on unsaturated acids and anhydrides, such as crotonic acid, cinnamic acid, and maleic anhydride. However, the reaction which takes place is not the simple peroxide-catalyzed reaction with the double bond mentioned above. Study of this reaction is being continued.

Experimental Part

Chlorination of Cyclohexene.—The chlorination of cyclohexene can be carried out most conveniently by adding the sulfuryl chloride through a condenser to the cyclohexene contained in a flask. It is advisable to use freshly-distilled cyclohexene, adding one or two drops of benzaldehyde or some similar peroxidic material (old cyclohexene, ascaridole) as a catalyst. The reaction is strongly exothermic and the use of a diluent (carbon tetrachloride, methylene chloride, or benzene) to moderate the vigor of the reaction is recommended.

It is also advantageous to use a comparatively volatile solvent and to keep the reaction mixture boiling gently in order to facilitate the escape of the sulfur dioxide from the solution. Otherwise, side reactions of the sulfur dioxide with the olefin decrease the yield.

In a round-bottomed flask fitted with a ground-glass joint were placed 24.6 g. of cyclohexene (0.3 mole) and 30 g. of carbon tetrachloride. The flask was attached to a reflux condenser, and a solution of 27.0 g. of sulfuryl chloride (0.2 mole) in 30 g. of carbon tetrachloride was then added gradually through the condenser in the course of an hour. The heat of the reaction is sufficient to keep the mixture refluxing. After all the sulfuryl chloride had been added, the reaction mixture was heated gently for another hour, and was then fractionated. There was isolated 27.2 g. of dichlorocyclohexane (b. p. 79–80° at 22 mm., n_D^{20} 1.4903). This represents a yield of nearly 90% (based on the sulfuryl chloride used).

Chlorination of Allyl Chloride.—The chlorination of allyl chloride is similar to that described above. Yields of 80 to 90% of 1,2,3-trichloropropane are readily obtained.

Chlorination of *sym*-Dichloroethylene.—The chloro derivatives of ethylene are comparatively insensitive to traces of peroxides. For this reason these compounds may be purified easily, and the dependence of the reaction of sulfuryl chloride with the double bond upon peroxide catalysis shown.

Freshly distilled dichloroethylene, b. p. 60–60.5° (19.4 g., 0.2 mole), and sulfuryl chloride (40.5 g., 0.3 mole) were heated under reflux for three hours in the dark. At the end of this time, the reaction mixture was fractionated: no reaction had taken place. The fractions were combined, a small quantity of benzoyl peroxide (0.002 mole) was added, and the refluxing was continued. Slow evolution of sulfur dioxide from the reaction mixture indicated that a reaction was now taking place. At the end of two hours the heating was discontinued, and the mixture was fractionated. There was isolated 29.5 g. of *sym*-tetrachloroethane (b. p. 143–145°, n_D^{20} 1.4942). The yield was 85%.

Chlorination of Stilbene.—In the absence of added peroxide, stilbene reacts slowly with sulfuryl chloride. Whether this slow reaction is due to a trace of peroxide, or whether it is a slow thermal bimolecular reaction, could not be determined. The addition of a small quantity of benzaldehyde or ascaridole brings about a rapid, vigorous reaction at room temperature. The yield of crude product (stilbene dichloride) is quantitative. After fractional crystallization of this crude material, first from alcohol to obtain the higher-melting isomer, and then from ligroin to obtain the other isomer, there was obtained a 45% yield of α, α' -stilbene dichloride, m. p. 191–193°, and a 33% yield of the β, β' isomer, m. p. 90–93°.

Chlorination of Tetraphenylethylene.—Tetraphenylethylene, like stilbene, reacts slowly with sulfuryl chloride in the absence of added peroxide. When a trace of a peroxide (benzaldehyde which

gives a strong peroxide test, or ascaridole) is added, the reaction is accelerated tremendously. The product formed is the dichloride, m. p. 184–186° (dec.).

Summary

1. Sulfuryl chloride reacts with ethylenic compounds to form the corresponding dichlorides. The following olefins have been chlorinated: cyclohexene, allyl chloride, dichloroethylene, tetrachloroethylene, stilbene, and tetraphenylethylene.

2. The chlorination of these ethylenic compounds by means of sulfuryl chloride is catalyzed by organic peroxides.

3. It is suggested that the reaction proceeds through a chain mechanism involving atoms and free radicals.

CHICAGO, ILLINOIS

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The Wound Hormones of Plants. IV. Structure and Synthesis of a Traumatin¹

BY JAMES ENGLISH, JR.,^{1a} JAMES BONNER AND A. J. HAAGEN-SMIT

Many plant tissue extracts are capable of inducing renewed growth activity in mature plant cells. These growth inducing extracts are usually obtained from ground or heated tissues, and they are capable of evoking cell division and cell enlargement in unwounded cells. The active principles have therefore been referred to as "wound hormones."² The present paper concerns the structure and synthesis of one highly active "wound hormone," 1-decene-1,10-dicarboxylic acid, whose isolation has already been announced.³ The authors propose that the name "traumatic acid" be used in referring to this substance.

In earlier papers⁴ a quantitative bio-assay (the bean test) for wound hormone activity has been described.

Activity tests of the material described below

(1) This paper describes work begun under a grant from the Lalor Foundation. Report of work carried out with the cooperation of the Works Progress Administration, Official Project Number 665-07-3-83, Work Project Number 9809.

(1a) Present address: Yale University, New Haven, Conn.

(2) (a) G. Haberlandt, *Beit. z. allgemeinen Botanik*, **2**, 1 (1921); (b) G. Haberlandt, *Biol. Zentr.*, **42**, 145 (1922).

(3) J. English, J. Bonner and A. Haagen-Smit, *Proc. Nat. Acad. Sci.*, **25**, 323 (1939).

(4) J. English and J. Bonner, *Jour. Biol. Chem.*, **121**, 791 (1937); J. Bonner and J. English, *Plant Physiol.*, **18**, 331 (1938).

were always carried out in the presence of a "co-factor"⁵ mixture.

One-tenth gamma of the pure substance per applied drop elicits a detectable response in the bean test. The pure product, m. p. 165–166°, is optically inactive and yielded an equivalent weight by titration of 118. A micro-Zerewitinoff determination carried out on the dimethyl ester showed the absence of active hydrogen. Catalytic hydrogenation yielded decane-1,10-dicarboxylic acid, identified by melting point and mixed melting point with an authentic sample prepared from decamethylene glycol.⁶

Since the analysis and the result of the hydrogenation experiment indicated the existence of one double bond, an oxidative degradation was carried out. On oxidation of the methyl ester with permanganate in acetone solution, sebamic acid was formed indicating the presence of a double bond in the α - β position. This conclusion was confirmed by the synthesis of 1-decene-1,10-di-

(5) For a description of the preparation and properties of this co-factor mixture, see note 3. Sucrose and particularly glutamic acid can in part replace the co-factor mixture in augmenting the activity of traumatic acid.

(6) P. Chuit, *Helv. Chim. Acta*, **9**, 264 (1926).