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

REACTIONS OF ATOMS AND FREE RADICALS IN SOLUTION. XXVIII. THE ADDITION OF N-CHLOROSULFONYLPHTHALIMIDE TO OLEFINS

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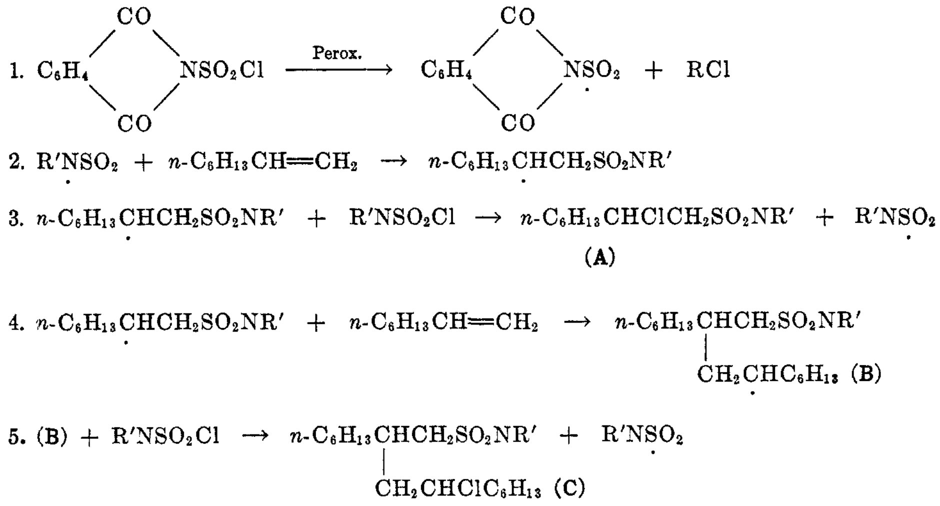
The reaction of a 1-alkene with sulfuryl chloride and a diacyl peroxide (trace) to give β-chloroalkyl sulfones was taken as evidence of the formation in the above reaction mixture of free $(SO_2Cl)\cdot$ radicals (1). It was of interest to ascertain whether the related free $(RNSO_2)\cdot$ radicals could be generated in solution, and whether these would add to olefins.

Addition of N-chlorosulfonylphthalimide to 1-alkenes. It was established that 1-decene and 1-octene and N-chlorosulfonylphthalimide do not react in the absence of a diacyl peroxide. However, when 1-decene and N-chlorosulfonylphthalimide are heated together at 125–130° in the presence of four mole-% of benxoyl peroxide a 64% yield of the one-to-one adduct is obtained, as well as eight % of a solid which has the elementary composition calculated for an adduct of two molecules of 1-decene and one of N-chlorosulfonylphthalimide. Similar results were obtained with 1-octene.

The adducts cited are probably formed as follows:



1. $C_6H_4(CO)_2NSO_2Cl \xrightarrow{\text{Perox.}} C_6H_4(CO)_2N\underset{\cdot}{SO_2} + RCl$

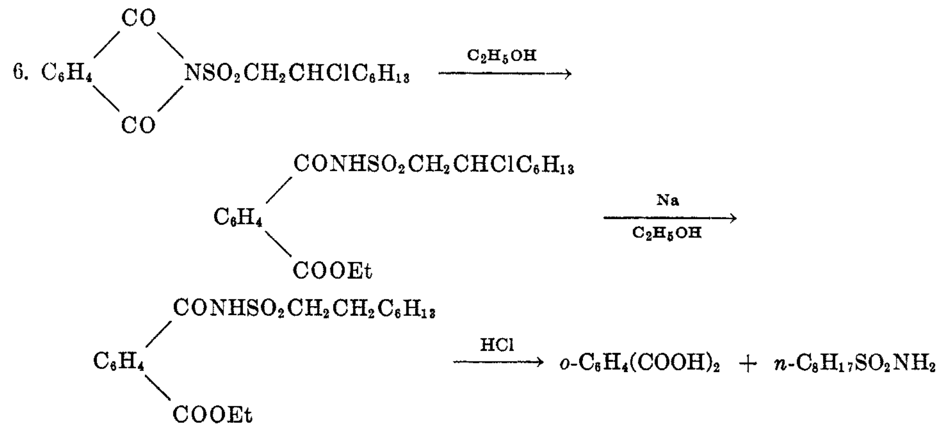
2. $R'\underset{\cdot}{N}SO_2 + n\text{-}C_6H_{13}CH{=}CH_2 \rightarrow n\text{-}C_6H_{13}\underset{\cdot}{C}HCH_2SO_2NR'$

3. $n\text{-}C_6H_{13}\underset{\cdot}{C}HCH_2SO_2NR' + R'NSO_2Cl \rightarrow \underset{\textbf{(A)}}{n\text{-}C_6H_{13}CHClCH_2SO_2NR'} + R'N\underset{\cdot}{SO_2}$

4. $n\text{-}C_6H_{13}\underset{\cdot}{C}HCH_2SO_2NR' + n\text{-}C_6H_{13}CH{=}CH_2 \rightarrow n\text{-}C_6H_{13}CH(CH_2\underset{\cdot}{C}HC_6H_{13})CH_2SO_2NR'$ (B)

5. (B) + $R'NSO_2Cl \rightarrow n\text{-}C_6H_{13}CH(CH_2CHClC_6H_{13})CH_2SO_2NR' + R'N\underset{\cdot}{SO_2}$ (C)

Proof of structure of adduct (A)—[*N-(2-Chloro-n-octyl)sulfonylphthalimide*]. The structure of adduct (**A**) was established as follows:



The phthalic acid was identified by conventional methods. The *n*-octanesulfonamide thus obtained did not depress the melting point of an authentic sample of that material prepared by conventional methods.

EXPERIMENTAL PART

Purification of materials. The olefins were fractionated prior to use (1-octene, Humphrey Wilkinson Inc., n_D^{20} 1.4089, b.p. 120.2°; 1-decene, Connecticut Hard Rubber Co., n_D^{20} 1.4223, b.p. 170–171°). The N-chlorosulfonylphthalimide used in this work melted at 157–158°.

Preparation of N-chlorosulfonylphthalimide (2). Sulfuryl chloride (54.8 g., 0.40 mole) and 150 ml. of benzene (dried over sodium wire) were placed in a one-liter three-necked flask equipped with a mercury-sealed stirrer, dropping-funnel, and a condenser. Anhydrous conditions were maintained by protecting all outlets to the external atmosphere with calcium chloride tubes. While the flask was cooled in an ice-bath (0–5°), potassium phthalimide (75.0 g., 0.40 mole), suspended in 450 ml. of dry benzene, was added during seven hours.

The solid material was collected and dried under a vacuum; additional solid was recovered by evaporation of the benzene solution under reduced pressure. The two solid fractions were combined and extracted with dry benzene, and the benzene solution was saturated with dry hydrogen chloride gas in order to decompose the N-chlorophthalimide formed in the reaction. After standing overnight, the phthalimide which separated was collected. Hydrogen chloride was removed from the filtrate at reduced pressure. The remaining benzene was distilled at atmospheric pressure. The N-chlorosulfonylphthalimide thus obtained (44.7 g.) melted at 154–157°. Upon crystallization from glacial acetic acid, the material melted at 157–158°.

Addition of N-chlorosulfonylphthalimide to 1-octene. A mixture of N-chlorosulfonylphthalimide (10 g., 0.041 mole) and 1-octene (18.2 g., 0.164 mole) was refluxed, and benzoyl peroxide (0.2 g., 2 mole-%) was added in several portions. The sulfonyl chloride, which was insoluble in boiling 1-octene, slowly dissolved (15 min.) to give a light-yellow colored solution. The hot solution was poured into 150 ml. of ligroin (100°), and the product that crystallized was collected (7.0 g., 48% yield). Crystallization of this material from ligroin gave a product which melted at 98–99°.

Anal. Calc'd for $C_{16}H_{20}ClNO_4S$: N, 3.9; S, 9.0; Cl, 9.9; Mol. wt., 358.
Found: N, 3.8; S, 9.2; Cl, 9.8; Mol. wt., 384.

The ligroin filtrate upon evaporation gave a viscous oil (4.8 g.). This material is probably the adduct of two molecules of 1-octene with one of N-chlorosulfonylphthalimide.

Anal. Calc'd for $C_{24}H_{36}ClNO_4S$: S, 6.8; Cl, 7.5.
Found: S, 5.8; Cl, 8.5.

Reactions of N-(2-chloro-n-octyl)sulfonylphthalimide. (*a*). The adduct (1 g.) was treated with 20 ml. of 5% sodium hydroxide solution and the whole gently warmed. The resulting solution was neutralized with dilute hydrochloric acid and the white oil which separated at first became solid upon standing (0.8 g.). After crystallization from benzene, the solid melted at 111–112°. The compound was soluble in sodium bicarbonate solution and decolorized an aqueous permanganate solution.

Anal. Calc'd for $C_{16}H_{21}NO_5S$: N, 4.1; S, 9.4.
Found: N, 4.2; S, 9.6.

(*b*) The adduct (2 g.) was refluxed with 40 ml. of absolute ethyl alcohol (99.5%) for four hours. Ethyl alcohol was removed by evaporation to give a viscous liquid. The addition of ligroin (60°) induced the oil to crystallize to a waxy solid (1.2 g.). Upon crystallization from ligroin, the compound melted at 82–83°.

Anal. Calc'd for $C_{18}H_{26}ClNO_5S$: N, 3.5; S, 7.9; Cl, 8.8.
Found: N, 3.8; S, 8.0; Cl, 8.9.

Addition of N-chlorosulfonylphthalimide to 1-decene. N-Chlorosulfonylphthalimide (3.0 g., 0.012 mole), 1-decene (6.8 g., 0.048 mole), and benzoyl peroxide (60 mg., 2 mole-%) were placed in a 100-ml. flask equipped with a condenser to which was attached a calcium chloride tube. The flask was immersed in an oil-bath maintained at 125–130°, and after ten minutes heating an additional 60 mg. of benzoyl peroxide was added. The sulfonyl chloride gradually dissolved, and after 25 minutes heating was discontinued. The hot reaction mixture was poured into 40 ml. of ligroin (60°), and the solid which separated was collected (m.p. 90–91°, 3.0 g., 64% yield).

Anal. Calc'd for $C_{18}H_{24}ClNO_4S$: N, 3.6; S, 8.3; Cl, 9.2.
Found: N, 3.9; S, 8.3; Cl, 9.0.

Evaporation of the ligroin-decene solution gave a sticky, viscous oil (1.9 g.). After standing for several days, this oil partially crystallized. It was treated with ligroin (30°), cooled in a Dry Ice-bath, and the solid which separated (0.4 g.) was collected. The product thus obtained (8.5% yield) melted at 68–69° and is probably the addition product of two molecules of 1-decene with one of N-chlorosulfonylphthalimide.

Anal. Calc'd for $C_{28}H_{44}ClNO_4S$: N, 2.7; S, 6.1; Cl, 6.7.
Found: N, 2.7; S, 6.2; Cl, 6.9.

Evaporation of the filtrate gave 1.3 g. of an oily residue.

Anal. Found: Cl, 7.6.

Proof of structure of N-(2-chloro-n-octyl)sulfonylphthalimide. Sodium (1.0 g.) was added in small pieces to a solution of the adduct (1.0 g.) in 25 ml. of absolute ethyl alcohol. The reaction mixture was heated on the steam-bath (1 hour), neutralized with dilute hydrochloric acid, and most of the alcohol was removed by heating on a steam-bath. The residue was extracted with ether, and the ether solution was washed with water and dried over calcium chloride. Evaporation of the ether gave an oil which was free of chlorine.

The oil was heated with 25% hydrochloric acid for 24 hours and unchanged material was collected. Upon overnight standing the filtrate deposited two types of crystals, namely, tiny "egg-like" pellets and shiny leaflets. The liquid and the shiny leaflets were separated from the heavy "egg-like" pellets by decantation. After washing with water, the "egg-like" pellets were collected (0.2 g.). They melted at 187° (dec.). Phthalic acid has m.p. 188° (dec.). These pellets were sublimed at 200° to give white needles which melted at 127.5–128.0°. The melting point of a mixture of the sublimate with an authentic sample of phthalic anhydride showed no depression.

The shiny crystals (0.1 g.) were separated from the liquid. Upon crystallization from an ether-ligroin mixture, they melted at 68–69°. This material did not depress the melting point of an authentic sample of *n*-octanesulfonamide.

Preparation of n-octanesulfonamide. n-Octanesulfonyl chloride was prepared by the method of Johnson and Sprague (3). *n*-Octyl bromide (30.6 g.) and thiourea (11.8 g.) were refluxed on a steam-bath with 25 ml. of ethyl alcohol until a test sample failed to give a precipitate of silver sulfide with ammoniacal silver nitrate (20 hours). Most of the alcohol was removed at reduced pressure, and the resulting oil (39 g.) crystallized when treated with ether. Further crystallization gave a substance which melted at 96–97°.

Anal. Calc'd for $C_9H_{21}BrN_2S$: N, 10.4. Found: N, 10.5.

The S-octylisothiourea hydrobromide was dissolved in 50 ml. of distilled water, and 50 ml. of a saturated solution of potassium acetate was added. A bulky white precipitate of the acetate was obtained which was collected and crystallized from 250–300 ml. of water; m.p. 129–130°.

Anal. Calc'd for $C_{11}H_{24}N_2O_2S$: N, 11.3. Found: N, 11.6.

The S-octylisothiourea acetate (10 g.) was suspended in 100 ml. of water maintained at 10°. Chlorine gas was bubbled into the mixture until the reaction was complete. The solution was extracted with ether, and the ether extract was washed with dilute sodium bisulfite solution and then with distilled water, and dried over calcium chloride. After removal of the ether, the sulfonyl chloride distilled at 115–116°/6 mm.

n-Octanesulfonamide was prepared by pouring the sulfonyl chloride into a concentrated solution of ammonium hydroxide. The resultant precipitate, after crystallization from an ether-ligroin mixture, melted at 70.0–70.5°.

Anal. Calc'd for $C_8H_{19}NO_2S$: N, 7.3; S, 16.6.
Found: N, 7.3; S, 16.6.

Attempts to extend the N-chlorosulfonylphthalimide reaction. No adduct was formed when N-chlorosulfonylphthalimide was treated with the following olefins (in the presence of a peroxide): styrene, indene, vinyl acetate, or allyl chloride. Varying amounts of a "polymeric" material were obtained. The N-chlorosulfonylphthalimide was recovered as well as small amounts of phthalimide.

No adduct was obtained when N,N-dimethylsulfamyl chloride or N,N-dimethylcarbamyl chloride were allowed to react with 1-octene in the presence of benzoyl peroxide.

SUMMARY

1. 1-Octene and 1-decene undergo a peroxide-induced reaction with N-chlorosulfonylphthalimide to give the corresponding N-(2-chloro-*n*-octyl)sulfonylphthalimide and N-(2-chloro-*n*-decyl)sulfonylphthalimide, respectively.

2. A reaction scheme to account for the products is outlined.

3. The present study provides evidence for the existence of a free radical of the type $(RNSO_2)\cdot$ and demonstrates its ability to react with 1-alkenes to give carbon to sulfur and not carbon to oxygen bonds.

4. The preparation of a number of new compounds is described.

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