Tetrahedron Letters No.17, pp. 1629-1632, 1967. Pergamon Press Ltd. Printed in Great Britain.

REARRANGEMENT OF N-CHLORO-N-ALKYL-ALKANESULFONAMIDES.

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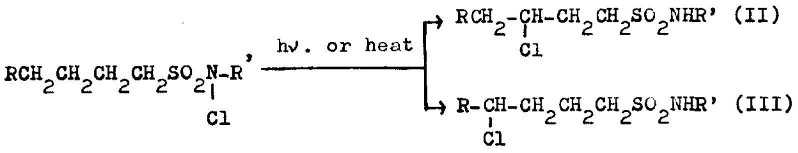
(Received 16 January 1967; in revised form 6 February 1967)

Recent publications on the free radical rearrangements of N-haloamides to the corresponding 4-haloamides (1,2,3,4,5) have prompted us to study the photo-rearrangement of N-chlorosulfonamides.

We have found that N-chloro-N-alkyl-alkansulfonamides (I) readily rearrange to the corresponding chloroalkane isomers, i.e. N-alkyl-γ-chloroalkanesulfonamides (II) and N-alkyl-δ-chloroalkanesulfonamides (III) under the influence of photo-irradiation or heat.



$$RCH_2CH_2CH_2CH_2SO_2\underset{Cl}{N}\text{-}R' \xrightarrow{h\nu\text{. or heat}} \begin{cases} RCH_2\text{-}\underset{Cl}{CH}\text{-}CH_2CH_2SO_2NHR' & \text{(II)} \\ R\text{-}\underset{Cl}{CH}\text{-}CH_2CH_2CH_2SO_2NHR' & \text{(III)} \end{cases}$$

(I)

(R : H or alkyl, R' : alkyl)

This reaction affords a promising method for the synthesis of sultam derivatives, since the formation of sultams by the alkali treatment of γ-chlorosulfonamides has recently been reported (8).

This communication describes the results obtained with N-chloro-N-t-butyl-n-butanesulfonamide, which was quantitatively synthesized by passing chlorine into an aqueous solution of the corresponding N-t-butyl-n-butanesulfonamides (b.p. 155 - 6° at 6mm, n_D^{20} 1.4530) in the presence of sodium hydroxide.

N-chloro-N-t-butyl-n-butanesulfonamide (n_D^{20} 1.4718, active chlorine (%), found 15.03, calc. 15.56) was irradiated with a high pressure mercury lamp (150W) in benzene solution (10.0g N-chloro-N-t-butyl-n-butanesulfonamide in 150g of benzene) at 10 - 15°C under nitrogen until the active chlorine content of the solution was negligible.

The active chlorine disappeared within 10 - 15 minutes and a pale yellow liquid (9.8g, chlorine content 12.05%) was obtained.

The analysis of this product by g.l.c. (Apiezon L grease 10% on Diasolid L. 60 - 80 mesh, 1m column, column temp. 200°) showed three major peaks. These peaks were shown to be N-t-butyl-n-butanesulfonamide (IV), N-t-butyl-γ-chlorobutanesulfonamide (V) and N-t-butyl-δ-chlorobutanesulfonamide (VI) respectively by means of a comparison of their retention times with those of the pure compounds (V, m.p. 62 - 3°, VI, m.p. 39.5°).

The content of each compound in the product was estimated by g.l.c. using N-methyl-propanesulfonamide (b.p. 158 - 159° at 7mm) as an internal standard, and it was found that the product contained 26.0% (IV), 60.9% (V) and 12.1% (VI).

When this product was treated with sodium hydroxide in methanol, the formation of five and six membered ring sultams was shown by g.l.c. analysis.

We also found that N-chloro-N-t-butyl-n-butanesulfonamide rearranged on heating up to 165°C under nitrogen without solvent to give 45.6% (V), 3.8% (VI) and 45.6% (IV).

In this reaction, however, the ratio of the δ-chloro to the γ-chloro compound (0.08) was smaller than that (0.2) observed when the dilute benzene solution of N-chloro-N-t-butyl-n-butanesulfonamide was irradiated.

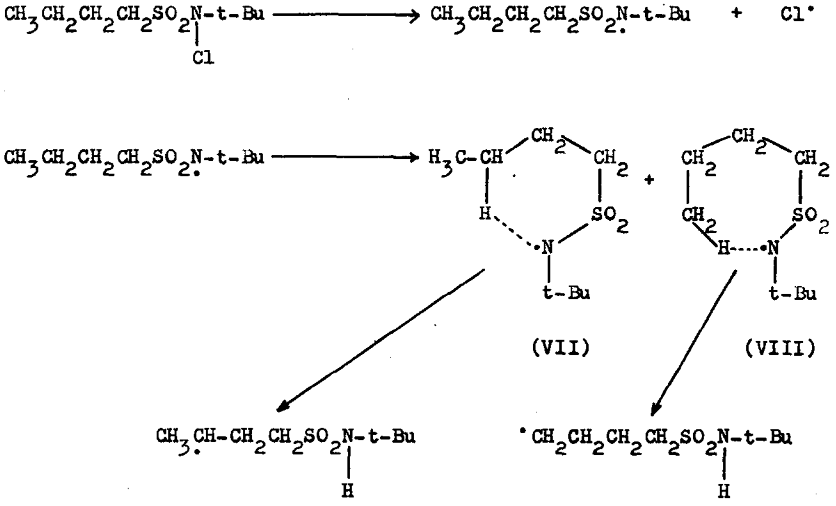
In addition, we investigated the photochlorination of N-t-butyl-n-butanesulfonamide (IV) in order to compare the hydrogen abstraction by the sulfonamide radical with that by the chlorine atom.

A benzene solution of N-t-butyl-n-butanesulfonamide (7.0g IV in 100g benzene) was irradiated for 30 minutes with gaseous chlorine (an equivalent quantity to

IV) at 10 - 15° and the reaction product was found to contain 16.0 % (V) and 1.6 % (VI) by g.l.c. analysis.

From the results obtained, the mechanism of the photo-rearrangement of N-chloro sulfonamides was considered to be analogous to that suggested by Neale (4) and Beckwith (3) for the photo-rearrangement of N-chloroamides.

The sulfonamide radical formed by the homolysis of the N-Cl bond was assumed to abstract γ- and δ-hydrogens of n-butyl group intramolecularly with the formation of a six membered (VII) or seven membered (VIII) transition states as shown below.



(VII) (VIII)

However, in the reaction initiated by thermal homolysis of N-chloro-N-t-butyl-n- butanesulfonamide without solvent, the intermolecular hydrogen abstraction by sulfonamide radical was supposed to occur competitively to an appreciable extent, because, in this reaction, N-t-butyl-n-butanesulfonamide was obtained in almost the same quantity as the rearranged products (V, VI) and the content ratio of VI to V was found to be very low, in accordance with the high reactivity of sulfonamide radical towards secondary hydrogens (6,7).

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