

THE REACTION OF N-CHLOROETHANESULFONAMIDE WITH 1-HEXENE

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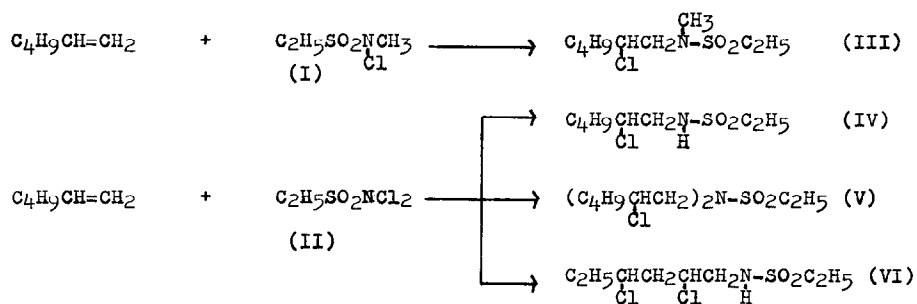
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The addition of N-aryl-N-halosulfonamides to styrene and cyclohexene was reported in earlier papers (1-4), but the mode of addition, isolation and analysis of all reaction products were not fully investigated. Recently a report concerning the allylic chlorination of internal monoolefinic compounds by N-aryl-N-chlorocyclohexylsulfonamide was published but it did not refer to adduct formation (5). The addition of N-haloalkanesulfonamides to long chain 1-olefins has not yet been reported. In this communication, results of the addition of N-chloro-N-methylethanesulfonamide (I) and N,N-dichloroethanesulfonamide (II) to 1-hexene are described.

I and II react with 1-hexene under photoirradiation to form addition products in anti-Markownikoff fashion. In the reaction of II, formation of N-(β,δ-dichlorohexyl)ethanesulfonamide and the 1:2 adduct occurred when excess (2.2mol) 1-hexene was employed (Scheme I).

Scheme I



I (20.0g, 0.13 mol) was added to 1-hexene (16.0g, 0.19 mol) and benzene (50g), and the solution was irradiated with a high pressure mercury lamp (150W) at 10-15° under nitrogen until the active chlorine content of the solution was negligible (450 min.). N-methyl-N-(β-chlorohexyl)ethanesulfonamide (III), (17.0g, 58 %, b.p 115°/0.03)

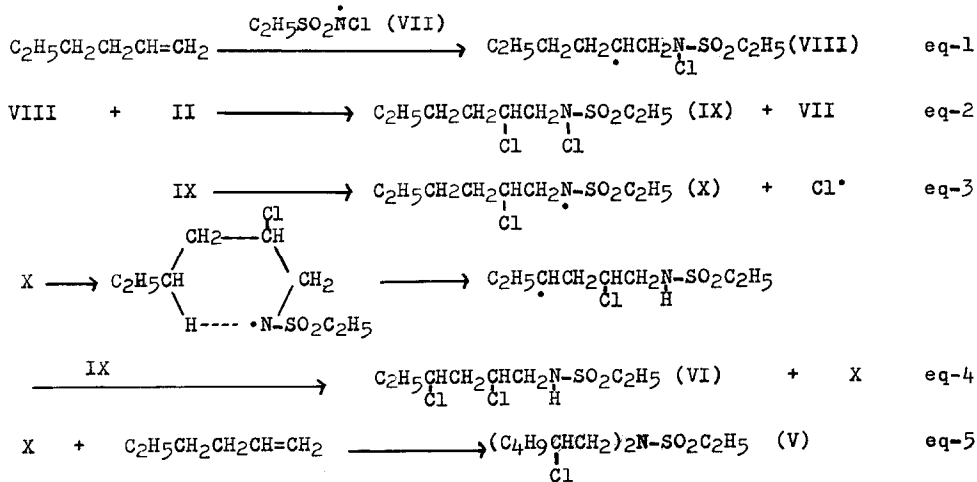
was isolated from the reaction product and its structure was confirmed by nmr.

In addition to III, N-methylethanesulfonamide (7.4g) and chlorides, a mixture of 1-chloro-2-hexene and 1,2-dichlorohexane, (1.9g) were obtained.

Reaction of N,N-dichloroethanesulfonamide (II) with 1-olefin was complicated. When II, (60.2g) and an equimolar quantity of 1-hexene (28.4g) were irradiated in benzene (80g) until the active chlorine content of the solution was reduced to one-half of its initial value (85min.), and the reaction product was treated with sodium bisulfite, N-(β-chlorohexyl)ethanesulfonamide (IV) (23.2g, m.p 47.5°) and N-(β,δ-dichlorohexyl)ethanesulfonamide (VI) (9.9g, m.p 93-4°) were isolated from the reaction product together with the by-products, ethanesulfonamide (10.5g) and chlorides (11.8g). The melting point of a mixture of IV and the authentic compound prepared from β-chlorohexylamine (6) and ethanesulfonyl chloride was not depressed.

In the reaction using an excess of 1-hexene (83.1g, 0.99mol) to II (80.0g, 0.45mol) in benzene (150g), the solution was irradiated until the active chlorine content became negligible (460min.). IV (30.4g), VI (38.4g) and N,N-bis-(β-chlorohexyl)ethanesulfonamide (V) (11.2g,  $n_D^{25}$  1.4780,) were obtained together with ethanesulfonamide (14.5g) and chlorides (25.5g). Reaction sequences to account for the formation of V and VI are shown in Scheme II.

Scheme II



The formation of ethanesulfonamide and 1-chloro-2-hexene may be explained by the

competitive allylic hydrogen abstraction from 1-hexene by VII, X or ethanesulfonamide radical ( $C_2H_5SO_2NH$ ). The mechanism of the formation of VI (eq-3,4) is assumed to be analogous to the rearrangement of N-chloro-N-alkylalkanesulfonamides (7). Although N-butyl-N-chloroarylsulfonamide was reported to rearrange to the N-6-chloro derivative in sulfuric acid (8), no report has been published on the analogous rearrangement of N-alkyl-N-chlorosulfonamides in benzene. The formation of V and VI and the absence of N-( $\alpha,\epsilon$ -dichloro-2-hexyl)ethanesulfonamide are supporting evidence that II adds to 1-hexene in anti-Markownikoff fashion and the intermediate IX is present in the reaction.

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