Conversion of *NN'*-Dialkylsulphamides into Azoalkanes. Formation of the Thiadiaziridine 1,1-Dioxide Ring System

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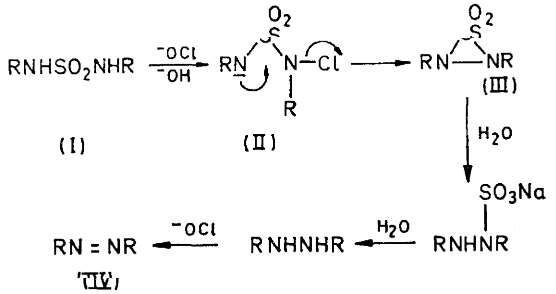
Summary *NN'*-Di-t-butylsulphamide is converted into *trans*-2,2'-dimethyl-2,2'-azopropane *via* the formation of an *N*-sulphamide anion and 2,3-di-t-butylthiadiaziridine 1,1-dioxide.

A SIMPLE synthesis of aliphatic azo-compounds involves treatment of *NN'*-dialkylsulphamides with alkaline sodium hypochlorite at 20—60°.[1] By contrast, *NN'*-diarylsulphamides under the same conditions afford quinone anils.[2] The suggested mechanism of the former reaction is shown in the Scheme. During the initial steps either a simple nitrogen anion or the equivalent chloronitrogen derivatives must be formed.

In order to study this useful preparative route in more detail, we sought to synthesize several of the proposed intermediates. Addition of t-butyl hypochlorite to (I; R = Bu^t) in methanol at room temperature produced (II; R = Bu^t) (80%); m.p. 100—102°; ν_{max} (KBr) 1393 and 1369 cm^{-1}; τ ($CDCl_3$) 1·52 and 1·38. Treatment of (II; R = Bu^t) with NaH in pentane, $KOBu^t$ in Bu^tOH, or aqueous NaOH gave (I; R = Bu^t), and traces of (III; R = Bu^t). The use of an excess of hypochlorite did not yield di-t-butyl-*NN'*-dichlorosulphamide, which is in agreement with earlier work.[2]

By contrast, if the sulphamide (I; R = Bu^t) was mixed with NaH (1 equiv.) in pentane at 0°, then the corresponding sodio-derivative was formed quantitatively; m.p. > 350°; ν_{max} (KBr) 1392 and 1369 cm^{-1}; τ (DMSO) 1·51 and 1·37. Addition of hypochlorite gave compound (III; R = Bu^t) (61%); m.p. 35–36°; ν_{max} (KBr) 1395 and 1372 cm^{-1}; τ ($CDCl_3$) 1·33. On prolonged refluxing in pentane or benzene the thiadiaziridine (III; R = Bu^t) smoothly rearranged to afford *trans*-(IV; R = Bu^t) and SO_2. However, *cis*-(IV; R = Bu^t), is unstable and decomposes at 0° to produce a complex hydrocarbon mixture. These data permit a tentative assignment of a *trans* configuration to (III); this is in accord with a similar analysis on *cis*- and *trans*-2,3-diphenylthiiran 1,1-dioxides.[4] Whether the transformation is a concerted or a radical process is uncertain.[5]



The structure assigned to (III) is supported by mol. wt. measurements, and by the formation of a Diels–Alder adduct with 1,3-diphenylisobenzofuran. Compound (III; R = Bu^t) is stable towards dilute acid or base. These results imply that under the above conditions the conversion of (I; R = Bu^t) into the azopropane (IV; R = Bu^t) is a stepwise process. Reaction in NaH–Bu^{t}OCl–pentane gives better yields than reaction in water.

The reported syntheses of (III; R = Bu^t and R = $-CMe_2CH_2CMe_3$)[6]† differs in detail from the one used by us, while the related *X*-ray data supports a *trans* configuration, at least for (III; R = $-CMe_2CH_2CMe_3$).

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