Diazoalkanes from Methylsulphinylhydrazones

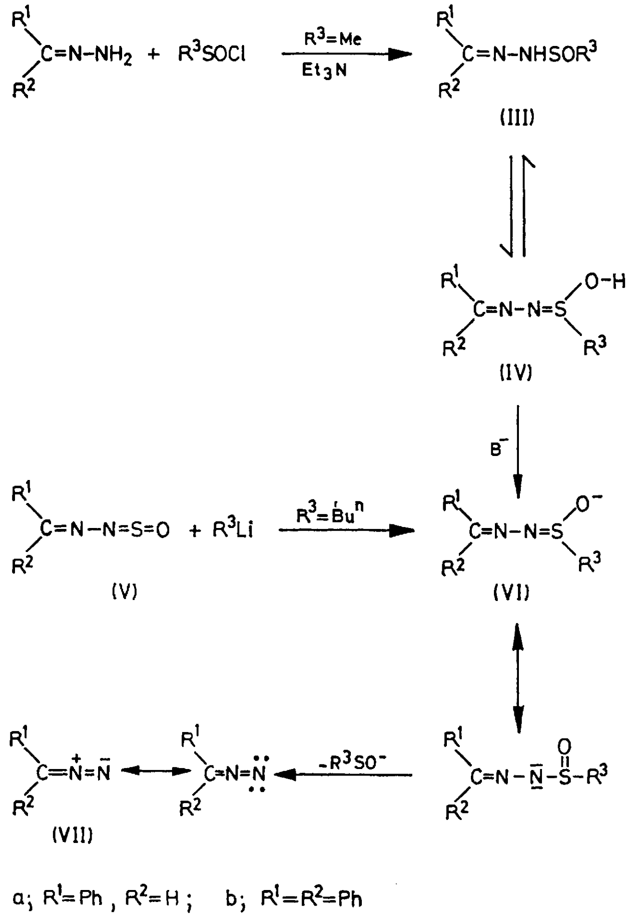
By James G. Shelnut, Shuntaro Mataka, and Jean-Pierre Anselme*

(*Department of Chemistry, University of Massachusetts at Boston, Boston, Massachusetts* 02125)

Summary Base-catalysed α-elimination of methylsulphenic acid from methylsulphinylhydrazones leads to aryldiazoalkanes; diphenyldiazomethane was also obtained from the reaction of $Ph_2C=N-N=S=O$ with butyllithium.

Recently, we reported formaldehyde *N*-methyl-*N*-phenylhydrazone (II) as one of the products of the decomposition of *N*-methyl-*N*-phenyl-*N'*-methylsulphinylhydrazone (I).[1] The formation of (II) was rationalized *via* a diazene–hydrazone rearrangement of *N*-methyl-*N*-phenyldiazene (*N*-nitrene). We now describe the generation of diazoalkanes

(VII), which can be considered as imino *N*-nitrenes, from the base-catalysed α-elimination reaction of methylsulphinylhydrazones (III).



Treatment of an ethereal solution of benzophenone hydrazone containing two equivalents of triethylamine at 0° with methylsulphinyl chloride gave a yellow solution which immediately began to turn pink. After overnight reflux, the red ethereal solution was separated from the precipitated triethylamine hydrochloride and washed with water. Evaporation of the dried solution left a red oil (60%)† whose i.r. spectrum was identical with that of an authentic sample of diphenyldiazomethane (VIIb). Similarly, phenyldiazomethane (VIIa) was obtained in 40% yield† from benzaldehyde hydrazone and methylsulphinyl chloride. Diazofluorene and $PhCOC(Ph)=N_2$, along with other products, were also formed in analogous reactions of fluorenone and benzil hydrazones, respectively.

When the reactions were carried out at −60°, the methylsulphinylhydrazones (IIIa) and (IIIb) were isolated. The n.m.r. and i.r. spectra of (IIIa) as well as combustion analysis results were consistent with the assigned structure. On pyrolysis or treatment with alcoholic alkali, phenyldiazomethane was formed. Although (IIIb) was too sensitive for elemental analysis, it gave diphenyldiazomethane on pyrolysis and on treatment with base.

N.m.r. data of sulphinylhydrazines bearing a hydrogen on the nitrogen attached to the sulphinyl group, indicate that these compounds exist as the iminosulphinic acid derivatives.[2] Since sulphinic acids are strong acids,[3] the ease of α-elimination in this case may be rationalized *via* the easy proton removal from the iminosulphinic acid tautomer (IV). Elimination of the methylsulphenate ion would then generate the diazoalkanes. In support of this, we have generated anion (VI, $R^1 = R^2 = Ph$) by the addition of (V)[4] to butyllithium at low temperature; diphenyldiazomethane (VIIb) formation was instantaneous and was indicated by the appearance of the deep wine-red colour. It was characterized by its i.r. spectrum and isolated in 35% yield as benzhydryl 3,5-dinitrobenzoate. No attempt was made to maximize the yield of these reactions.

We thank the National Institute of Health for partial support of this work.

(*Received, 5th November* **1974**; *Com.* **1350**.)

---

† Yield determined by the formation of the 3,5-dinitrobenzoate.

[1] S. Mataka and J.-P. Anselme, *J.C.S. Chem. Comm.*, 1974, 554.

[2] Part III of this series, S. Mataka and J.-P. Anselme, submitted for publication.

[3] F. Wudl, D. A. Lightner, and D. J. Cram, *J. Amer. Chem. Soc.*, 1957, **89**, 4099; A. Senning, O. N. Sorensen, and C. Jacobsen, *Angew. Chem. Internat. Edn.*, 1968, 734.

[4] A. Senning, *Rec. Trav. chim.*, 1963, **82**, 790; D. Klamann, U. Kramer, and P. Weyerstahl, *Chem. Ber.*, 1962, **95**, 2694.