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CHEMICAL SYNTHESIS OF CIS-AZOISOPROPANE

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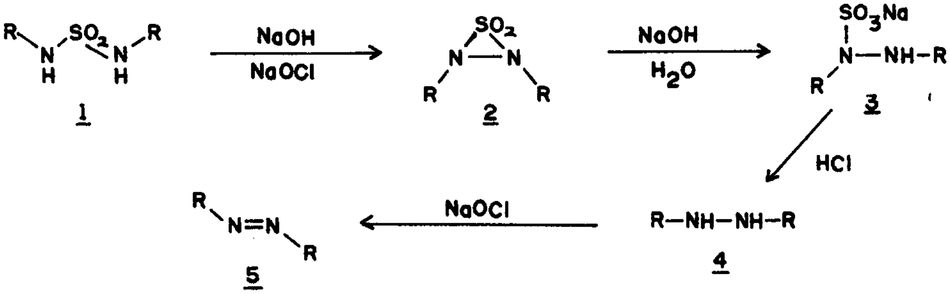
The most general method for preparation of trans azoalkanes is hypochlorite oxidation of sulfamides, a procedure pioneered by Ohme and co-workers.[1] Only two acyclic cis azoalkanes, azomethane and azoisopropane (AIP, 5 R = iso-C_3H_7), have been isolated and both were made by irradiating the trans isomer in solution.[2-4] These compounds are of considerable interest for spectroscopic,[5] thermochemical,[6] and photochemical[7] studies.



Although the Ohme method is successful for a wide variety of azoalkanes, its application to azoisopropane has never been reported. In fact the published procedure[1] gives a 28% yield of trans AIP, which is about half of that obtained with other azoalkanes. However, it was interesting to note that ether extraction of the solution containing 3 before acidification led to the isolation of a small amount of yellow oil consisting of both cis and trans AIP, as shown by vpc. Since it was easily demonstrated that hypochlorite oxidation of 4 gave only trans AIP, it seemed possible that the small amount of cis obtained arose directly from the thiadiaziridine dioxide 2. It has now been found that mild reaction conditions allow oxidation of 1 to a mixture of cis and trans AIP in satisfactory yield. The use of potassium carbonate as base presumably circumvents ring opening of 2 and permits its transformation to the azoalkane. A similar reaction has been reported[8] between bis (1,1,3,3-tetramethylbutyl)thiadiaziridine-1,1-dioxide and t-butyl hypochlorite but only the trans azoalkane was obtained. The absence of cis azo-t-octane may be due to its extreme thermal lability.

The preparation of cis azoisopropane is carried out as follows. Diisopropyl sulfamide (mp 104.5-106.5°) is synthesized in 75% yield by the procedure of Stowell.[9] A 27.6 g (0.2 mol) portion of anhydrous potassium carbonate is dissolved in 278 cc (0.2 mol) of household bleach (5.5 % NaOCl, 0.72 M) and this solution is added slowly with good stirring to 18.0 g (0.1 mol) diisopropyl sulfamide in 200 cc of methylene chloride. The mixture is refluxed and stirred magnetically for 20 hours or until potassium iodide-starch test paper is no longer turned purple. After removal of the methylene chloride by distillation at 760 mm, vpc analysis of the yellow residue shows that the ratio of cis to trans AIP is 0.65. The cis isomer tends to tautomerize to the hydrazone on storage but this process is very slow at -78°. Since the boiling point of cis AIP (66°/77 mm) is much higher than that of trans, separation of the isomers can be achieved by vacuum bulb-to-bulb distillation into a U-shaped trap cooled to -78°. The progress of the distillation is readily monitored by vpc (6', 10% SF-96, 120°), the retention time of cis being about 60% greater than that of trans.[10] Bulb-to-bulb distillation of the residue provides cis AIP of 95% purity.[11] Although conventional distillation of this material generally leads to considerable tautomerization, the trans AIP can be purified in this manner, bp 88.5°/760 mm. The combined yield of both isomers is 67%

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References and Footnotes

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