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FLASH VACUUM PYROLYSIS OF α-TOLUENESULFONYL AZIDE

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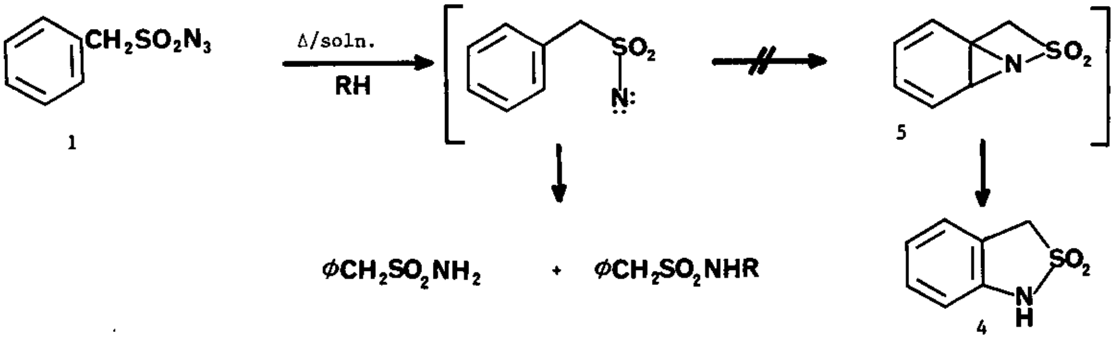
Abstract - The flash vacuum pyrolysis of α-toluenesulfonyl azide (1) gave bibenzyl (2), 2-(β-phenethyl)pyridine (3), and 2,1-benzisothiazole 2,2-dioxide (4); an authentic sample of the latter was prepared from 2-bromo-α-toluenesulfonamide and potassium amide in liquid ammonia. FVP of benzenesulfonyl azide using benzene as carrier gas gave some diphenylamine, but not in the absence of benzene.

A recent report[1] describing the first synthesis of the parent 2,1-benzisothiazole 2,2-dioxide ring system (4) prompts us to report hitherto unpublished results. Some years ago[2] we found that thermolysis of α-toluenesulfonyl azide (1) in dodecane gave α-toluenesulfonamide (26.5%) and N-dodecyl-α-toluenesulfonamide (41.8%) but no 4, and we proposed that geometrical restrictions did not permit the formation of the required aziridine intermediate (5)[3] in this case, so that intermolecular reactions competed very favorably. We reasoned that if all intermolecular competition was eliminated some 5 would be formed and 4 would result. This now proves to be the case and we report the flash vacuum pyrolysis (FVP) of 1 under various conditions and the remarkable formation of 3.



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FVP of 1 in a static system at 350°C (inlet temperature 123°C, initial pressure 10μ, contact time 0.32 sec) gave bibenzyl (2)(4.7%), mp 52°C, identical with an authentic sample, 2-(β-phenethyl)pyridine (3)(6%), bp 67-68°C/22μ, and 2,1-benzisothiazole 2,2-dioxide (4)(5%), mp 126-126.5°C. The mixture was resolved by chromatography on a column of neutral alumina. Authentic 3 was prepared by catalytic hydrogenation[4] of 2-styrylpyridine[5]. Authentic 4 was synthesized (51% yield) via the aryne intermediate generated from 2-bromo-α-toluenesulfonamide, mp 118.5-119.5° C ($CHCl_3$) [itself prepared (33% yield) from sodium 2-bromo-α-toluenesulfonate, mp 285°C and thionyl chloride in CCl_4 containing some DMF] and potassium amide in liquid ammonia.

The results of the FVP carried out under a variety of conditions, including the introduction of possible trapping agents, are summarized in the Table.

Table. FVP of α-toluenesulfonyl azide

Oven temp. (°C)	P (Torr)	Products (%) 2	3	4
350[a]	2[b]	5.2	7.6	4.1
360[c]	2.5-3[b]	5.7	2.3	4.3
390[a]	2[b]	8.1	6.0	1.7
450[a]	3.10^{-2}	2.2	3.8	0.9
450	2.5-3[b]	10.5	1.5	
500	3[b]	13.0	1.1	

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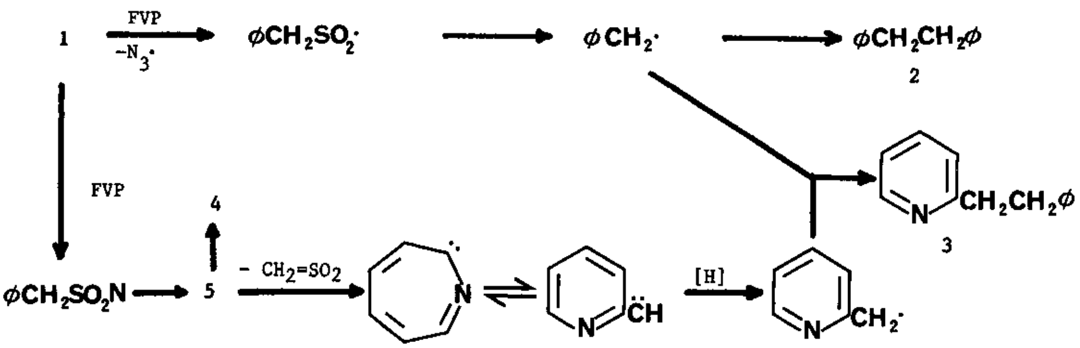
[a] With benzene on the cold finger. [b] N_2 as the carrier gas. [c] Gaseous methanol introduced as trapping agent.

The formation of 2 is readily explained in terms of a homolysis[6] of 1 to $PhCH_2SO_2\cdot$ and $\cdot N_3$ followed by loss of SO_2 to give $PhCH_2\cdot$ and dimerization of the latter, probably on the cold finger. Sultam 4 is probably formed via the highly strained benzaziridine 5 as discussed above. The latter could also lead to 3 as follows: elimination of sulfene $CH_2=SO_2$ would lead to azacycloheptatrienylcarbene (6) whose ring-contraction in the gas phase to 2-pyridylcarbene is well established.[7] Hydrogen-abstraction would lead to the 2-picolyl radical which would combine with $PhCH_2\cdot$ on the cold finger to yield 3.



Sulfene is known to react with MeOH in the gas phase to give $MeSO_2OMe$.[8] When methanol was introduced as a trapping agent in the FVP (Table) no methyl sulfonate or formaldehyde dimethyl acetal (possible loss of SO from sulfene followed by trapping with MeOH) could be detected by TLC. Considerable amounts of tar were formed, however, so that this absence of trapping does not necessarily eliminate the proposed pathway to 3. Coating the cold finger with benzene did not lead to any trapped nitrene product.[9]

The use of a carrier gas (higher pressure) decreases the pumping speed and thereby increases the lifetime of the molecules in the hot zone of the pyrolysis tube and this, together with higher pyrolysis temperatures, seems to favor the radical cleavage rather than nitrene formation.

ACKNOWLEDGEMENT

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9. Phenylnitrene, generated by the FVP of $PhSO_2N_3$ ($PhSO_2N \rightarrow PhN{=}SO_2 \rightarrow PhN + SO_2$) at 450 C and 0.2 Torr inlet pressure and using benzene as carrier gas, was trapped by the benzene to give diphenylamine (2.9%), in addition to azobenzene (36.7%), biphenyl (1.9%), and tar. In the absence of benzene no Ph_2NH or Ph-Ph were detected. This is in contrast to the observations of Renfrow and Devadoss[10] who observed more Ph_2NH in the absence of C_6H_6 than in its presence on gas phase pyrolysis of $PhSO_2N_3$.

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