

Reactive Intermediates. Part XIX.¹ The Lithium Salt of 1-(Benzotriazol-1-yl)-4-*p*-tolylsulphonyltetrazene: a New Benzyne Precursor

By M. Keating, M. E. Peek, C. W. Rees,* and R. C. Storr, The Robert Robinson Laboratories, University of Liverpool, Liverpool L69 3BX

The lithium salt obtained from the monoanion of 1-aminobenzotriazole and toluene-*p*-sulphonyl azide is isolable, but gives benzyne immediately when dissolved in tetrahydrofuran or acetonitrile.

THE nitrene (1) generated by oxidation of 1-aminobenzotriazole with lead tetra-acetate fragments cleanly to give benzyne in high yield.² 1-Azidobenzotriazole would therefore be an ideal benzyne precursor since production of the latter would involve no other reactant and nitrogen would be the only other product.

Few *N*-azido-compounds are known. The production of *N*-azidobis(trimethylsilyl)amine³ and *N*-azidodimethylamine⁴ has been reported from the reactions of lithium and sodium azide, respectively, with the appropriate *N*-chloro-amines. However treatment of 1-chlorobenzotriazole with azide ion under a variety of conditions gave no azidobenzotriazole or products which could be ascribed to its breakdown. Azide ion was merely oxidised to nitrogen. This was not unexpected in view of the high positive halogen character of 1-chlorobenzotriazole.⁵ Aryl and alkyl azides have been obtained by treatment of the complex salts formed from Grignard reagents and toluene-*p*-sulphonyl azide with sodium pyrophosphate.⁶ Benzotriazolylmagnesium iodide, however, again gave no azidobenzotriazole with these reagents.

Anselme and his co-worker⁷ have shown that the monoanions of 1,1-disubstituted hydrazines (2) on treatment with toluene-*p*-sulphonyl azide give products resulting from the *N*-nitrene (3). It is not clear whether the *N*-nitrene arises *via* an unstable *N*-azide or directly from the pentazene salt (4).

Addition of an ethereal solution of toluene-*p*-sulphonyl azide to a solution of the monoanion of 1-aminobenzotriazole in tetrahydrofuran immediately gave a yellow precipitate which we assume to be the lithium salt (5).† No trace of an *N*-azido-compound was detected by solution i.r. spectroscopy. The lithium salt could be filtered off and washed with dry ether, but became *extremely unstable* when dry, decomposing unpredictably and spontaneously; in our experience, however, decomposition was not violent on the scale used.‡ When moist with dry ether the salt can be handled relatively safely and can be stored overnight without deterioration under ether.

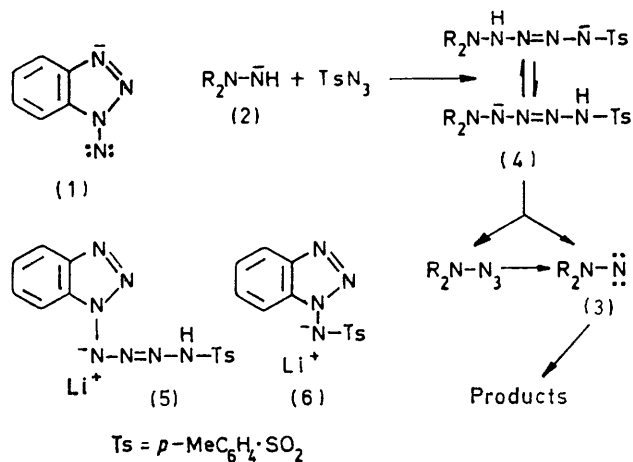
† Owing to its instability, elemental analysis of this compound was not possible.

‡ Extreme caution should be exercised in handling this compound and the scale should be kept to the minimum; we have not prepared the salt from more than 0.67 g (5 mmol) of 1-aminobenzotriazole.

§ The salt does not decompose appreciably in mixtures of tetrahydrofuran and ether, as used in its preparation, presumably because of insufficient solubility.

¹ Part XVIII, C. W. Rees and M. Yelland, *J.C.S. Perkin I*, 1972, 77.

When the salt is added to a polar aprotic solvent such as acetonitrile or, better, tetrahydrofuran, in which it has appreciable solubility,§ it decomposes rapidly at or below room temperature to give lithium toluene-*p*-sulphonamidate, nitrogen, and benzyne. Thus in tetrahydrofuran containing tetracyclone (3 equiv.),



tetraphenylnaphthalene is obtained in 65% yield. Under similar conditions in acetonitrile the yield is 45% and in dimethylformamide only 19%. The high rate of decomposition of the salt is indicated by the unusually high yield (44%) of biphenylene isolated from decomposition in the absence of a trap. This suggests that relatively high local concentrations of benzyne are involved. In protic solvents such as water or methanol, decomposition again occurs very readily, giving nitrogen and lithium toluene-*p*-sulphonamidate. Surprisingly, no phenol or anisole was detected, although benzyne was generated, as evidenced by the formation of 1-phenylbenzotriazole when the decomposition was carried out in methanol containing phenyl azide.

The Table summarises our results with a variety of benzyne traps. The yields compare favourably with those from other benzyne precursors, and while this

² C. D. Campbell and C. W. Rees, *J. Chem. Soc. (C)*, 1969, 742, 748, 752.

³ N. Wiberg and A. Gieren, *Angew. Chem. Internat. Edn.*, 1962, **1**, 664.

⁴ H. Bock and K. L. Kompa, *Angew. Chem. Internat. Edn.*, 1962, **1**, 264.

⁵ C. W. Rees and R. C. Storr, *J. Chem. Soc. (C)*, 1969, 1474, 1478.

⁶ P. A. S. Smith, C. D. Rowe, and L. B. Bruner, *J. Org. Chem.*, 1969, **34**, 3430.

⁷ G. Koga and J.-P. Anselme, *J. Org. Chem.*, 1970, **35**, 960, and references therein.

Generation of benzyne from the tetrazene salt (5) ^a				
Trap (mmol)	Solvent ^b (ml)	Product	Yield (%)	
Tetraphenylcyclopentadienone (15)	MeCN (10)	Biphenylene	44	
	THF (40)	1,2,3,4-Tetraphenyl-naphthalene	65	
	MeCN (40)		45	
	DMF (40)		19	
Methyl 2-oxopyran-5-carboxylate (9) Furan (20)	THF (15)	Methyl 2-naphthoate	67	
	THF (10)	1,4-Epoxy-1,4-dihydronaphthalene	10	
		1-Naphthol	31	
Toluene- <i>p</i> -sulphonyl azide (15)	THF (30)	1- <i>p</i> -Tolylsulphonylbenzotriazole	51	
Phenyl azide (15)	THF (15)	1-Phenylbenzotriazole	43	
Phenyl azide (20)	MeOH (40)	1-Phenylbenzotriazole	15	
Vinyl acetate (20)	MeCN (20)	Benzocyclobutenyl acetate	9	

^a In each case the tetrazene salt produced from 1-aminobenzotriazole (5 mmol) was decomposed. ^b THF = tetrahydrofuran; DMF = dimethylformamide.

method would normally be a less convenient route to benzyne from 1-aminobenzotriazole than oxidation by lead tetra-acetate, it does have the advantage that a powerful oxidant is excluded. Its advantage over other intramolecular benzyne precursors is the low temperature required for decomposition. It is interesting to compare the thermal stability of the salt (5) with that of the lithium salt of 1-*p*-tolylsulphonamidobenzotriazole (6), which is thermally very stable. The latter can be decomposed photochemically to give benzyne, but in lower yield.⁸

The very instability of the salt (5) is a practical disadvantage, and some effort was made to vary the cation and the amide leaving group in the hope of obtaining an analogous salt of more convenient stability. However the monolithium salt of 1-aminobenzotriazole did not react with benzoyl azide or *p*-nitrophenyl azide, and 1-benzotriazol-1-ylaminomagnesium iodide did not give a salt analogous to (5) with toluene-*p*-sulphonyl azide.

The foregoing method of generating nitrenes may be generally applicable to those heterocyclic *N*-nitrenes which fragment; thus 2-aminobenzotriazole gives *cis,cis*-hexa-2,4-dienedinitrile (1,4-dicyanobuta-1,3-diene) (40%) and 1-amino-4,5-diphenyltriazole gives diphenylacetylene (63%). These yields are to be compared with yields of 60%² and 80%,⁹ respectively, from direct oxidation with lead tetra-acetate, and of 98%² and 93%⁹ with iodobenzene diacetate. 1-Amino-3-phenylindazole is converted into 4-phenylbenzo-1,2,3-triazine, although in lower yield (34%) than by oxidation (80%),¹⁰ showing that the method also applies to some nitrenes which rearrange. In all these cases the intermediate salt does not separate out but decomposes *in situ*. No success was obtained, however, with those *N*-amino-compounds such as *N*-aminophthalimide which give rigid, non-fragmenting nitrenes.¹¹

EXPERIMENTAL

Lithium Salt of 1-(Benzotriazol-1-yl)-4-p-tolylsulphonyl-tetrazene (5).^{*}—Butyl-lithium (5 mmol) in ether or hexane was added to a stirred solution of 1-aminobenzotriazole²

(5 mmol) in dry tetrahydrofuran (5 ml) at room temperature under nitrogen. The colour of the solution changed from orange to red when the addition was complete. Toluene-*p*-sulphonyl azide (5 mmol) in ether (10 ml) was then added dropwise to give a yellow precipitate. The mixture was stirred for 0.5 h,[†] and dry ether (40 ml) was added to aid removal of the tetrazene salt by filtration. The salt was removed carefully in plastic apparatus, washed several times with dry ether, and used immediately.

Generation of Benzyne from the Tetrazene Salt (5).—The salt (5) was added in portions to a stirred solution of the trap in tetrahydrofuran, acetonitrile, or dimethylformamide at room temperature. When nitrogen evolution had ceased, most of the lithium toluene-*p*-sulphonamide was removed by filtration (the remainder of the toluene-*p*-sulphonamide was obtained in the subsequent chromatography of the filtrate). Other products were obtained from the filtrate by evaporation and chromatography of the residue. Results and conditions are summarised in the Table. In all cases benzyne adducts were compared directly with authentic specimens. Percentage yields are based on the amount of 1-aminobenzotriazole (5 mmol) originally taken.

cis,cis-Hexa-2,4-dienedinitrile.—Butyl-lithium (2.5 mmol) was added to 2-aminobenzotriazole² (2.5 mmol) in tetrahydrofuran (4 ml) at -30° to give a deep red solution. Addition of toluene-*p*-sulphonyl azide led to immediate evolution of nitrogen but no precipitate of 'tetrazene salt'. After stirring for 1 h at room temperature, the mixture was filtered and evaporated and the residue was chromatographed on silica gel to give the dinitrile (40%),¹² m.p. and mixed m.p. 123–125°, and a trace of the *cis,trans*-isomer (t.l.c. comparison with authentic specimen).

Diphenylacetylene.—1-Amino-4,5-diphenyltriazole⁹ (2.5 mmol) was treated exactly as described for 2-aminobenzotriazole. The final chromatography gave diphenylacetylene (63%), m.p. and mixed m.p. 59–60°.

4-Phenylbenzo-1,2,3-triazine.¹⁰—1-Amino-3-phenylindazole¹⁰ (2.5 mmol) was treated exactly as described for 2-aminobenzotriazole. Final chromatography (elution with ether) gave 4-phenylbenzo-1,2,3-triazine (34%), m.p. 153–154° (Found: C, 75.5; H, 4.6; N, 20.25. C₁₃H₉N₃ requires C, 75.35; H, 4.4; N, 20.3%), ν_{\max} (Nujol) 1610, 1565, 1390, 1362, 930, 780, and 704 cm⁻¹, λ_{\max} 206 (log ϵ 3.86), 232 (4.1), and 293 nm (2.95), *m/e* 207, 179, and 152.

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* See footnote p. 1315.

† See footnote p. 1315.

⁸ F. Graveling, Ph.D. Thesis, University of Leicester, 1969.

⁹ J. Adamson Ph.D. Thesis, University of Leicester, 1967.

¹⁰ D. J. C. Adams, S. Bradbury, D. C. Horwell, M. Keating, C. W. Rees, and R. C. Storr, *Chem. Comm.*, 1971, 828.

¹¹ D. J. Anderson, T. L. Gilchrist, D. C. Horwell, and C. W. Rees, *J. Chem. Soc. (C)*, 1970, 576.

¹² P. Kurtz, *Annalen*, 1960, **631**, 38.