LEAD TETRAACETATE OXIDATION OF A COMPOUND THAT IS SIMULTANEOUSLY A 1- AND A 2-AMINOBENZOTRIAZOLE[†]

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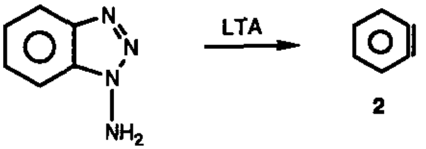
Abstract - Lead tetraacetate oxidation of bis-aminotriazole (**8**) in the presence of dienone (**11**) gave dinitrile (**12**) in good yield. Possible mechanisms are briefly discussed.

Oxidation of 1-aminobenzotriazole (**1**) with lead tetraacetate (LTA) provides a useful source of benzyne (**2**).[1,2] On the other hand, oxidation of 2-aminobenzotriazole (**3**) with LTA leads instead to *cis, cis*-muconitrile (**4**).[2] Both aminotriazoles may be formed on direct amination of benzotriazole, and both oxidations are thought to proceed via nitrene intermediates.



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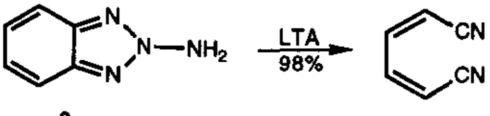

3 **4**

We have described the amination of 1,5-dihydrobenzo[1,2-*d*:4,5-*d'*]bistriazole (**5**), which gave a mixture of 1,5-, 1,7- and 1,6-diamino derivatives (**6**-**8**, respectively).[3,4] Both **6** and **7**, on oxidation with

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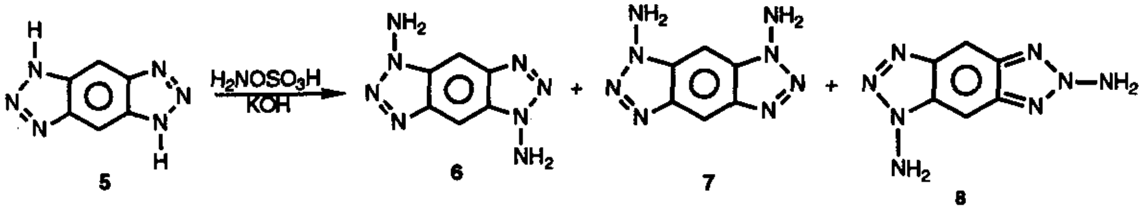
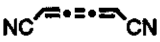
[†] This paper is dedicated to Professor Alan Katritzky on the occasion of his 65th birthday, with best wishes to him and Linde for many years of good health and fun with chemistry.



LTA, were synthetically useful equivalents of 1,4-benzadiyne.[3] It seemed of interest to examine the LTA oxidation of **8**, which is simultaneously a 1- and a 2-aminobenzotriazole. If oxidation were to occur at both aminotriazole moieties, one might anticipate novel products such as **9**[5-7] and/or its dimer (**10**).



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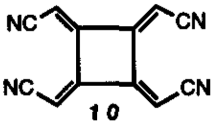
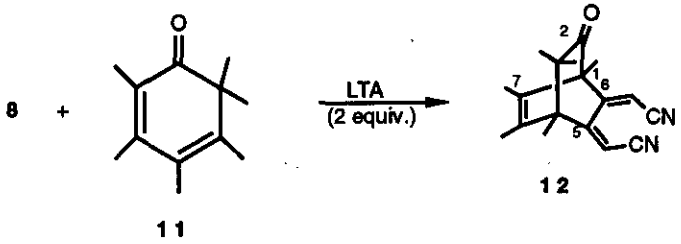


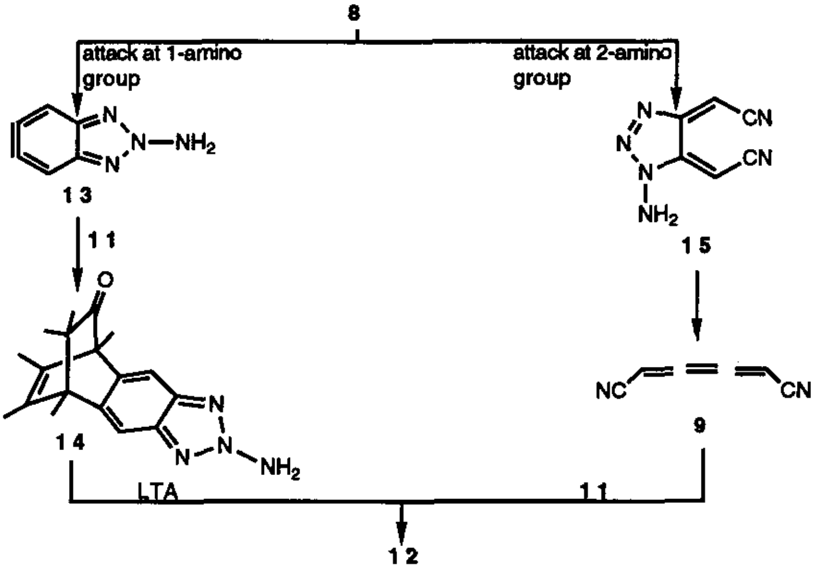
Oxidation of **8** with two equivalents of LTA at room temperature in tetrahydrofuran (THF) led only to a polymeric oil from which no well-defined product could be isolated. However, when the oxidation was carried out in the presence of one equivalent of hexamethyl-2,4-cyclohexadienone (**11**) as an aryne trap,[8] a crystalline product was obtained in 81% yield, assigned structure (**12**).



The infrared spectrum of **12** showed both carbonyl (1740 cm^{-1}) and cyano (2215 cm^{-1}) bands. The ^1H Nmr spectrum had peaks at δ 1.70 and 1.77 for the two homoallylically coupled methyl groups ($J \approx 1$ Hz), singlets at δ 1.41 and 1.45 for the bridgehead methyls and at δ 0.89 and 1.09 for the *gem*-dimethyl group, as well as singlets at δ 5.62 and 5.66 for the vinyl protons. The ^{13}C Nmr spectrum was consistent with the structure (see Experimental Section). The mass spectrum showed, in addition to the M^+ peak at *m/z* 280, a base peak at *m/z* 210 corresponding to the loss of dimethylketene. This is a predominant process in many such bicyclo[2.2.2]octenones. The stereochemistry of the double bonds in **12** was not determined but is assigned by analogy with the oxidation of **3** to **4**.

Possible routes to **12** are summarized in Scheme 1. If oxidation of the 1-aminotriazole moiety occurs first, aryne (**13**) should be generated. This would cycloadd to **11** to give **14** which, with a second equivalent of LTA would give **12**. Less precedented and perhaps less likely would be the route via initial attack at the 2-aminotriazole moiety. This could afford bisalkylidenetriazole (**15**) and dicyanobutatriene (**9**)[5] which might then cycloadd to **11** to give **12**. One might be able to decide between these two alternatives by using only one equivalent of LTA; if the oxidation rate of **14** were considerably slower than that of the 1-aminotriazole moiety of **8**, one might isolate intermediate (**14**). Similarly for the alternative route to **12**, one might be able to isolate **15**[9].

Scheme 1



EXPERIMENTAL SECTION

Oxidation of 8. To a stirred mixture of **8** (0.56 g, 2.95 mmol) in 100 ml of dry THF under argon was added 2.9 g (6.5 mmol) of LTA in portions, over 30 min. After 5 min additional stirring, the lead diacetate was filtered and the filtrate was diluted with water (500 ml) and extracted with methylene dichloride (3 x 100 ml). The combined extracts were washed successively with saturated aqueous $NaHCO_3$, saturated aqueous NaCl and dried

($MgSO_4$). Removal of the solvent gave only 0.17 g of a polymeric oil from which no pure compound could be isolated.

1,3,3,4,7,8-Hexamethyl-5,6-bis(cyanomethylene)-bicyclo[2.2.2]oct-7-en-2-one (12). To a mixture of **8** (0.62 g, 3.26 mmol) and dienone **11**[10] (0.58 g, 3.26 mmol) in 100 ml of dry THF at room temperature was added 3.2 g (7.21 mmol) of LTA in portions over 30 min. Workup as above, followed by chromatography of the residue on silica gel using 3:1 chloroform-hexane as eluent gave 0.74 g (81%) of **12** as a white solid, mp 368-369 °C. ^{1}H Nmr ($CDCl_3$): see text; ^{13}C nmr ($CDCl_3$) δ 199.50 (C=O), 161.28, 155.75, 139.52, 129.98, 116.54, 115.87, 98.06, 96.13 (6 vinyl and 2 nitrile carbons), 60.06, 52.24, 45.71 (C1, C3 and C4), 23.58 (2 overlapped signals), 14.25, 13.90, 11.99, 11.62 (6 methyl carbons); mass spectrum, *m/z* (relative intensity) 280 (trace), 210 (100), 195 (17), 183 (9), 168 (10), 153 (4); ir (KBr) 3025, 2970, 2930, 2870, 2215, 1740, 1590, 1440, 1385, 1270 cm^{-1}; high resolution mass spectrum: Calcd for $C_{18}H_{20}N_2O$: 280.1575; Found: 280.1582. *Anal.* Calcd: C, 77.11; H, 7.19; N, 9.99. Found: C, 77.39; H, 7.25; N, 10.22.

ACKNOWLEDGEMENT

We thank the National Institutes of Health (GM15997) for financial support of this research.

REFERENCES AND NOTES

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2. R. W. Hoffman "Dehydrobenzene and Cycloalkynes," Academic Press, New York, **1967**, p. 81.
3. H. Hart and D. Ok, *J. Org. Chem.*, 1986, **51**, 979.
4. The two possible *mono*amination products were also formed and could be recycled to produce additional **6-8**.
5. Triene (**9**) is apparently unknown, though its isomers ethenylidenepropanedinitrile[6][$CH_2=C=C(CN)_2$] and 1,1-dicyano-2-cyclopropene[7] are known.
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7. E. Ciganek, *J. Am. Chem. Soc.*, 1966, **88**, 1979.
8. Dienone (**11**) is an effective aryne trap in the reaction of **6** with LTA; D. Ok and H. Hart, *J. Org. Chem.*, 1987, **52**, 3835.

9. Unfortunately an oxidation with only one equivalent of LTA was not carried out, and due to retirement (H. H.) we are not able to carry out further work on this problem. Others are welcome.
10. H. Hart, R. M. Lange and P. M. Collins, *Org. Synth.*, Coll. Vol. V, J. Wiley and Sons, New York, **1973**, p. 598.

Received, 23rd July, 1993