

LEAD TETRAACETATE OXIDATION OF 3-AMINO-9-CYANAZULENO[2,1-d]TRIAZOLE
AND 1-AMINO-9-CYANAZULENO[1,2-d]TRIAZOLE.
A NOVEL OXIDATIVE CLEAVAGE OF AMINOTRIAZOLE RING

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Summary: Either 1-amino-4-cyanazuleno[2,1-d]triazole or 3-amino-4-cyanazuleno[1,2-d]triazole reacts with lead tetraacetate in dichloromethane to give the unexpected ring cleavage product, 1,8,8-tricyanoheptafulvene in good yield instead of the expected 1-cyano-2,3-dehydroazulene.

It is generally accepted that oxidation of 1-aminobenzotriazole with lead tetraacetate does indeed constitute an efficient route leading to dehydrobenzene intermediate.¹⁾ Analogous oxidation of 2-aminobenzotriazole, however, leads to product derived from the di-imene intermediate and forms no dehydrobenzene.²⁾ The former method has successfully been applied to the generation of a novel dehydroaromatics, 4,5-dehydrotropone, which could be trapped with anthracenes,³⁾ cyclohexa-1,3-diene,⁴⁾ cyclopentadiene,⁴⁾ oxepine,⁵⁾ fulvenes,⁶⁾ and furans.⁷⁾

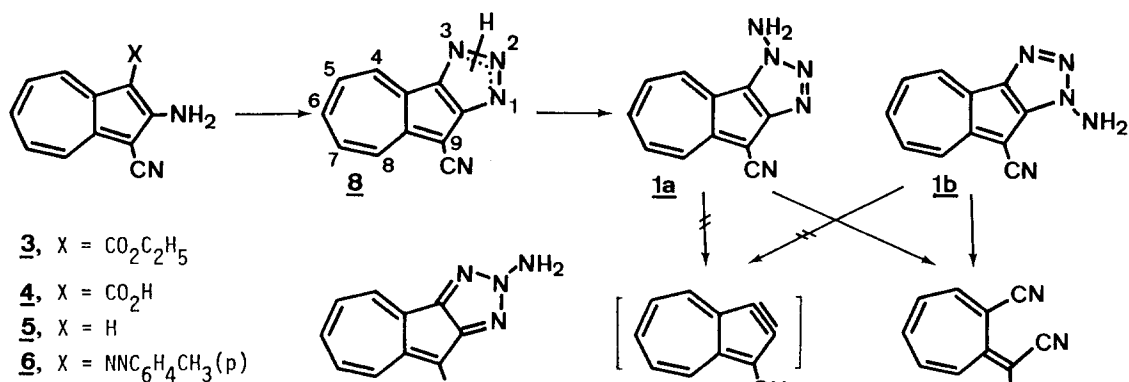
We now report the lead tetraacetate oxidation of aminotriazoles condensed with the five-membered ring of 1-cyanazulene such as 3-amino-9-cyanazuleno[2,1-d]triazole (1a) and 1-amino-9-cyanazuleno[1,2-d]triazole (1b) which might be expected to undergo decomposition to give 1-cyano-2,3-dehydroazulene (9). To examine this possibility, 1a and 1b were prepared by the sequence of reactions shown in Scheme I.⁸⁾ Hydrolysis of 2-amino-3-cyano-1-ethoxycarbonylazulene (3)⁹⁾ (KOH in C₂H₅OH, reflux for 4 h) gave the carboxylic acid 4 quantitatively which on decarboxylation (reflux in pyridine for 4 h) to give 2-amino-1-cyanazulene (5) in 73% yield. Azo-coupling of 5 with p-tolyldiazonium chloride gave 6 in 89% yield. Catalytic reduction of 6 (5% Pd/C, in CH₃COOC₂H₅) gave quantitatively the diamino derivative 7 as its hydrochloride, which, without purification, on diazotization (NaNO₂/HCl in aq. dioxane) gave 9-cyanazuleno[2,1-d]triazole (8) (or 9-cyanazuleno[1,2-d]triazole, mp 120 -

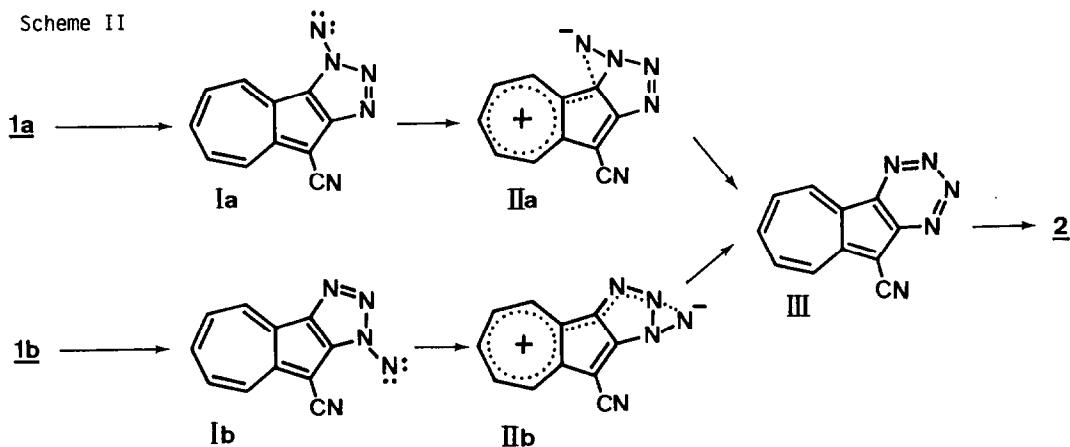
130 °C (decomp.), in 77% yield. The uv-visible spectrum of 8 [λ_{\max} in MeOH nm (log ϵ) 238 (4.11), 299 (4.54), 312 (4.54), 377 (3.78), 401 (3.84), 480 ~ 510 (2.69 ~ 2.65)] shows characteristic absorptions for azulene chromophore. Final conversion of 8 into a 3 : 2 mixture of 1a [reddish brown needles, mp 130 - 170 °C (decomp.), MS m/z 209 (M^+), ν 3290, 3160, 2210 cm^{-1}], and 1b [brown needles, mp 130 - 160 °C (decomp.), MS m/z 209 (M^+), ν 3310, 3130, 2190 cm^{-1}] which could be separated by silica gel column chromatography with dichloromethane and ethyl acetate (1:1 to 2:1), was performed in a 54% yield by treatment with sodium hydride in dimethylformamide followed by O-amino-2,4-dinitrophenol. The uv-visible spectra of 1a [λ_{\max} in MeOH nm (log ϵ) 235 (sh, 4.08), 314 (4.59), 387 (3.80), 405 (sh, 3.76), 480 ~ 510 (sh, 2.69 ~ 2.65)] and 1b [λ_{\max} in MeOH nm (log ϵ) 240 (sh, 4.02), 299 (4.54), 311 (sh, 4.49), 377 (3.79), 397 (3.84), 520 (2.41)] are closely similar to that of 8 suggesting that the azulene conjugations in 1a and 1b are remained intact [see Figure 1]. Although the alternate 2-amino-9-cyanazuleno[1,2-d]triazole structure (1c) could easily be ruled out by the above spectral consideration, the distinction between 1a and 1b is still obscure.¹⁰⁾

In order to examine the formation of 1-cyano-2,3-dehydroazulene (9), 1a (105 mg, 0.5 mmol) was oxidized in dichloromethane (100 mL) with lead tetraacetate (266 mg, 0.6 mmol) in the presence of large excess of cyclohexa-1,3-diene (1.9 mL, 40 equiv.). Despite careful examination of the reaction mixture, no expected trapping product of 9 by cyclohexa-1,3-diene could be detected. Instead the reaction yielded recovered cyclohexa-1,3-diene quantitatively and red crystalline product 2 in 83% yield, which was also available from 1b in

86% yield by the same oxidation. The structure of 2 was unambiguously deduced as 1,8,8-tricyanoheptafulvene from the elemental analysis [Found: C, 74.08, H, 2.76, N, 23.18. Calcd for $C_{11}H_5N_3$: C, 73.73, H, 2.81, N, 23.45] and spectroscopic properties [dark red plates, mp 111 - 111.5 °C, MS m/z 179 (M^+ , 100%); ν ($C\equiv N$) 2210 cm^{-1} ; λ_{\max} in MeOH nm (log ϵ) 234 (4.05), 262 (4.01), 373 (4.20)

Scheme I





[see Figure 2]; ^1H NMR (CDCl_3 , 400 MHz) δ 7.543 (dd, H-2, $J_{2,3} = 8.06$, $J_{2,4} = 0.98$ Hz), 7.293 (dt, H-6, $J_{6,5} = 11.72$, $J_{6,4} = J_{6,3} = 1.22$ Hz), 7.183 (ddt, H-4, $J_{4,3} = 10.74$, $J_{4,5} = 7.81$, $J_{4,6} = J_{4,2} = 0.98$ Hz), 7.021 (ddd, H-5, $J_{5,6} = 11.72$, $J_{5,4} = 7.81$, $J_{5,3} = 1.22$ Hz), 6.970 (ddt, H-3, $J_{3,4} = 10.74$, $J_{3,2} = 8.06$, $J_{3,5} = J_{3,6} = 1.22$ Hz)] compared with those of 8,8-dicyanoheptafulvene.¹¹⁾

Although 1,8,8-tricyanoheptafulvene (2) could arise in several ways, the formation of 2 can be rationalized by the assumption (Scheme II) that the initially generated nitrene intermediates (Ia, Ib) undergo ring opening through zwitter ions (IIa, IIb) to give the 1,2,3,4-tetrazine (III) which is ultimately decomposed to 2 with loss of a nitrogen. Reactions involving the oxidative ring expansion of 1- and 2-aminoindazole to 1,2,3-benzotriazine by lead tetraacetate are known¹²⁾ and provide good analogy for the above suggestion.

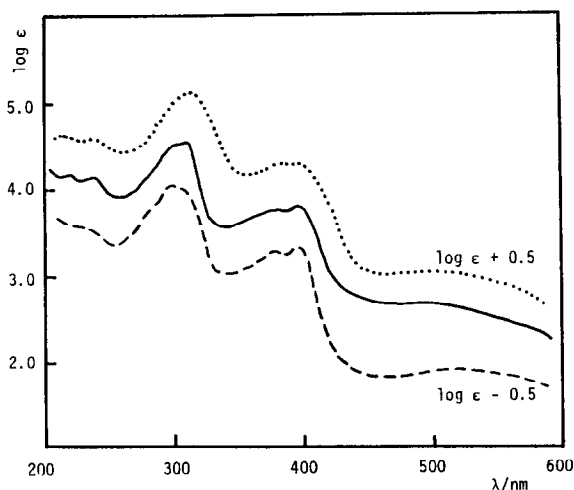


Figure 1. Electronic spectra of 1a (····), 1b (----), and 2 (—) in methanol.

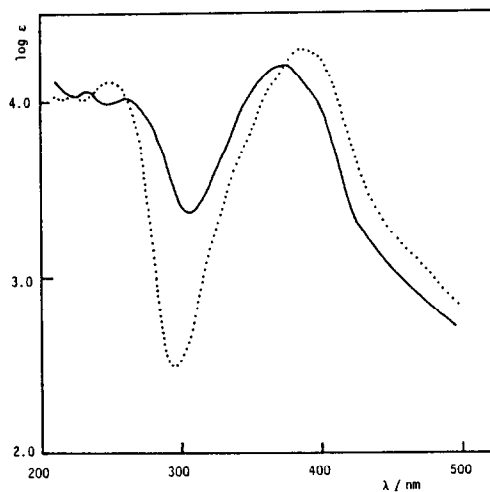


Figure 2. Electronic spectra of 8,8-dicyanoheptafulvene (····), and 2 (—) in methanol.

References

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(Received in Japan 4 October 1984)