1170. *Polycyclic Cinnoline Derivatives. Part XIV.*[1] 4,5,9-*Triazapyrene* (*quinolino*[5,4,3-cde]*cinnoline*), 4,5,9,10-*Tetra-azapyrene* (*cinnolino*[5,4,3-cde]*cinnoline*), *and their Oxides.*

By P. F. Holt and R. Oakland.

The preparations of 4,5,9-triazapyrene and 4,5,9,10-tetra-azapyrene and their oxides are described and their ultraviolet spectra are discussed.

Ruby[2] and Braithwaite, Holt, and Hughes[3] applied more than a dozen methods to the reduction of 2,2′,6,6′-tetranitrobiphenyl in attempting to produce 4,5,9,10-tetra-azapyrene (I).

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[1] Part XIII, P. F. Holt and C. W. Went, *J.*, 1963, 4099.

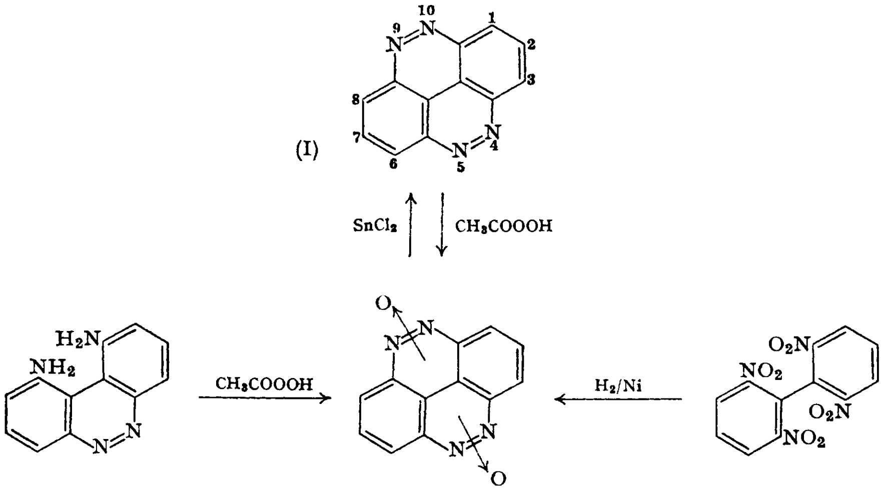
[2] Ruby, Ph.D. Thesis, University of Iowa, 1953.

[3] R. S. W. Braithwaite, P. F. Holt, and A. N. Hughes, *J.*, 1958, 4073.

The only products they could isolate were 2,2′-diamino-6,6′-dinitrobiphenyl, 2,2′,6,6′-tetra-aminobiphenyl, and polymeric azo-compounds. 4,5,9,10-Tetra-azapyrene was first prepared from tetranitrobiphenyl by Stetter and Schwarz[4] by catalytic hydrogenation under alkaline conditions at atmospheric pressure. Later Holt and Hughes[5] synthesised the tetra-azapyrene ring system by oxidising 1,10-diaminobenzo[*c*]cinnoline with peracetic acid. This method yielded the di-*N*-oxide. The reduction of this compound yielded a very small quantity of a substance which may have been the cinnoline, but its structure was in doubt. The ultraviolet absorption spectrum of this compound did not correspond to that published by Stetter and Schwarz.

We repeated the hydrogenation of tetranitrobiphenyl under the conditions given by Stetter and Schwarz and confirmed that the tetra-azapyrene ring system is formed. We produced the cinnoline only after hydrogenation, for about 24 hours; after about 5 hours the di-*N*-oxide was the sole product. The arrest of the hydrogenation seems to be due to coating of the catalyst. For reduction beyond the stage of the oxide it is necessary to make repeated additions of fresh catalyst. The rate of hydrogenation will, of course, depend on the activity of the catalyst, and that of Stetter and Schwarz may have been different from our own, but it would seem that these workers in fact produced both tetra-azapyrene and its di-*N*-oxide* since the ultraviolet absorption spectrum which they published corresponds to that of our di-*N*-oxide but the published analytical figures and properties correspond to the cinnoline we have prepared from it. The ultraviolet spectra of the di-*N*-oxide which was prepared by Holt and Hughes[5] and the compound formed by reducing it correspond to, respectively, those of the di-*N*-oxide and the tetra-azapyrene which we have prepared. There can be little doubt therefore that the substance described by Holt and Hughes was 4,5,9,10-tetra-azapyrene.

4,5,9,10-Tetra-azapyrene is oxidised by peracetic acid to a di-*N*-oxide (II) and the latter is reduced by stannous chloride back to the tetra-azapyrene. Both the tetra-azapyrene and its oxide give a colour test if suspended in alcohol and treated with sodium amalgam, when the yellow colour changes to green. The colour reverts to yellow when the sodium amalgam is removed. This was described by Stetter and Schwarz[4] as a test for tetra-azapyrene.



(I)

(II)

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* Analyses of a sample subsequently provided by Professor Stetter proved that it was essentially tetra-azapyrene dioxide.

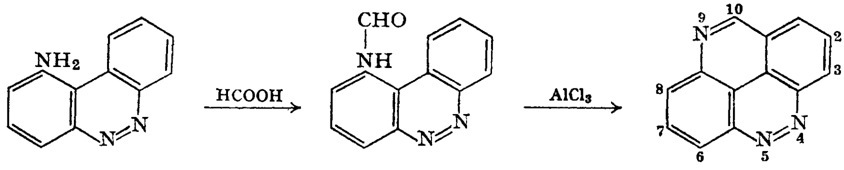
[4] H. Stetter and M. Schwarz, *Chem. Ber.*, 1957, **90**, 1349.

[5] P. F. Holt and A. N. Hughes, *J.*, 1960, 3216.

*Tetra-azapyrene Di-*N*-oxide and its Infrared Absorption Spectrum.*—Under some conditions the reduction of 2,2'-dinitrobiphenyl gives benzo[*c*]cinnoline 5,6-dioxide. It is conceivable, therefore, that the reduction of the tetranitrobiphenyl might produce tetra-azapyrene 4,5-, 4,9-, or 4,10-dioxide. Benzo[*c*]cinnoline di-*N*-oxide cannot, however, be formed by the oxidation of benzo[*c*]cinnoline and, since we have found that the tetra-azapyrene di-*N*-oxide can be formed by oxidation of the cinnoline, it is unlikely that it is the 4,5-dioxide.

The infrared absorption spectrum of the dioxide produced from the tetranitrobiphenyl differs very slightly from that of the dioxide formed by the oxidation of the cinnoline. Both spectra have twin peaks at 1417 and 1428 cm.$^{-1}$ where N–O is likely to absorb but these are much more intense in the former spectrum. A peak at 805 cm.$^{-1}$ (3 adjacent CH groups) in the former spectrum is shifted by +11 cm.$^{-1}$. A possible explanation of this anomaly is that one compound is the 4,9- and the other the 4,10- dioxide.

Triazapyrene.—The cyclisation of 2,2'-formamidobiphenyl has been used[6] to form 4,9-diazapyrene. We have cyclised 1-formamidobenzo[*c*]cinnoline (III) in an aluminium chloride–sodium chloride melt to produce 4,5,9-triazapyrene (IV). This new cinnoline derivative shows absorption peaks at 808 cm.$^{-1}$ (3 adjacent CH groups) and at 856 cm.$^{-1}$ (lone CH). It is oxidised by peracetic acid to a monoxide. Since all known cinnolines in which there is no steric hindrance around the nitrogen give a monoxide with peracetic acid, oxidation at the diaza-group is most probable. The oxide is thus 4,5,9-triazapyrene 4(?5)-oxide.



(III) (IV)

Ultraviolet Absorption Spectra.—Like their carbocyclic analogues, the non-linear polycyclic cinnolines show[7] three main regions of absorption (groups I, II, and III). Another band in the spectra of the cinnolines due to n–π* transitions can be demonstrated only when the cinnoline is in non-polar solvents;[8] tetra-azapyrene is insoluble in non-polar solvents. A band at shorter wavelengths (β') appears[9] in the spectrum of pyrene. Replacement of single methine groups by nitrogen has little influence on the positions of these main absorption bands (see the Table) but a diaza-group shifts the group II and III bands considerably to longer wavelengths. Aza-groups increase the intensity of the group III band and reduce the fine structure throughout the spectrum.[8,10] In agreement with this there are bathochromic shifts in the group II and III bands of the spectrum of 4,5,9-triazapyrene and still larger shifts in that of 4,5,9,10-tetra-azapyrene. Fine structure is lost and the intensity of the group III band is increased.

The changes in the spectra previously observed[11,12] when polycyclic cinnolines are converted into *N*-oxides are also observed in tri- and tetra-azapyrene spectra, *i.e.*, a large bathochromic shift of the group II and III bands and a large increase in intensity of the group III bands. The positions of the group II bands of the oxides are obscure but the shifts of the group III bands of tri- and tetra-azapyrene are clearly 22 and 29 mμ, respectively.

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[6] G. M. Badger and W. F. H. Sasse, *J.*, 1957, 4.
[7] A. E. Braude, *Ann. Reports*, 1945, **42**, 123.
[8] G. M. Badger and I. S. Walker, *J.*, 1956, 122.
[9] E. Clar, "Aromatische Kohlenwasserstoffe," Springer-Verlag, Berlin, 1952.
[10] G. M. Badger, R. S. Pearce, and R. Pettit, *J.*, 1951, 3199.
[11] J. F. Corbett, P. F. Holt, and A. N. Hughes, *J.*, 1961, 1363.
[12] K. E. Calderbank and R. J. W. Le Fèvre, *J.*, 1951, 649.

Values of $\lambda_{\text{max.}}$ (mμ) and (log ε) for pyrene and some aza-derivatives in ethanol.

	β′	I	II	III
Pyrene	231 241 (4·65) (4·92)	251 262 272 (4·08) (4·4) (4·70)	292(s) 305 318 334 (3·67) (4·07) (4·48) (4·66)	352 356 362 372 (2·70) (2·60) (2·58) (2·40)
4,9-Diazapyrene[6]	236 (4·85)	256 268 (4·32) (4·4)	305 318 330 (4·12) (4·18) (4·24)	344 352 362 370 (3·77) (3·82) (3·63) (4·02)
4,5,9-Triazapyrene	235 (4·73)	251 269 (4·19) (4·07)	347 (4·10)	367(s) 380 (3·85) (3·76)
4,5,9,10-Tetra-azapyrene	227(s) 235 (4·5) (4·68)	254(s) 263 (4·13) (4·21)	340 349(s) (4·22) (4·21)	373 380(s) 391 (3·79) (3·58) (3·87)
4,5,9-Triazapyrene oxide	223 236 (4·45) (4·47)	280 288 (4·13) (4·21)	358(s) 363 368(s) 382 402 (3·97) (4·00) (3·96) (4·00) (3·97)	
4,5,9,10-Tetra-azapyrene dioxide	222 (4·52)	267(s) 281 (4·16) (4·17)	314 327 358 398 420 (3·92) (3·95) (3·93) (3·98) (3·97)	

EXPERIMENTAL

4,5,9,10-*Tetra-azapyrene Di*-N-*oxide and* 4,5,9,10-*Tetra-azapyrene*.—2,2′,6,6′-Tetranitrobiphenyl (2 g.) and freshly activated Raney nickel were suspended in a mixture of ethanol (200 ml.) and 1M-sodium hydroxide solution (0·46 ml.). The mixture was hydrogenated at atmospheric pressure and room temperature until 1·06 l. of hydrogen had been absorbed. The precipitate was filtered off and extracted with hot dimethylformamide. On cooling, the extract yielded a yellow powder which crystallised from dimethylformamide as yellow needles of 4,5,9,10-tetra-azapyrene di-*N*-oxide (0·25 g.), decomp. > 270° (lit., decomp. 270°) (Found: C, 60·4; H, 2·7; N, 22·9. Calc. for $C_{12}H_6N_4O_2$: C, 60·5; H, 2·5; N, 23·5%).

When the procedure was continued until, even on addition of extra catalyst, no more hydrogen was taken up, the product, worked up as above, was obtained as pale brown needles of 4,5,9,10-tetra-azapyrene (0·2 g.), decomp. 270° (lit., decomp. 250°) (Found: C, 69·3; H, 3·1; N, 27·2. Calc. for $C_{12}H_6N_4$: C, 69·9; H, 2·9; N, 27·2%.)

Reduction of 4,5,9,10-*Tetra-azapyrene Di*-N-*oxide*.—Tetra-azapyrene di-*N*-oxide (0·3 g.), hydrochloric acid (*d* 1·18; 150 ml.), and stannous chloride dihydrate (1·1 g.) were heated on a water-bath for 45 min. The deep-blue liquid was poured into an excess of aqueous sodium hydroxide. A dark feathery precipitate of tetra-azapyrene formed which was filtered off and crystallised from dimethylformamide, forming pale brown needles (0·2 g.), decomp. > 270°. Its ultraviolet and infrared absorption spectra were identical with those of tetra-azapyrene prepared from 2,2′,6,6′-tetranitrobiphenyl.

Oxidation of 4,5,9,10-*Tetra-azapyrene*.—4,5,9,10-Tetra-azapyrene (98 mg.) was suspended in glacial acetic acid (20 ml.).—Hydrogen peroxide (80—90% w/w; 4 ml.) was added (most of the 4,5,9,10-tetra-azapyrene dissolved), followed by a trace of sulphuric acid. The blue mixture was filtered and the filtrate was left at room temperature overnight. The colour changed to red, and brown crystals formed which were filtered off and crystallised from dimethylformamide to yield yellow needles (30 mg.) of 4,5,9,10-tetra-azapyrene di-*N*-oxide, decomp. > 270° (lit., decomp. > 270°) (Found: C, 60·3; H, 2·4; N, 23·8. Calc. for $C_{12}H_6N_4O_2$: C, 60·5; H, 2·5; N, 23·5%). A second crop of di-*N*-oxide was deposited from the filtrate after a further week.

1-*Formamidobenzo*[c]*cinnoline*.—1-Aminobenzo[*c*]cinnoline, prepared by the method of Barton and Cockett,[13] was converted into 1-*formamidobenzo*[c]*cinnoline* (77%), m. p. 265—267° (Found: C, 69·2; H, 3·9; N, 19·2. $C_{13}H_9N_3O$ requires C, 69·9; H, 4·1; N, 18·8%).

4,5,9-*Triazapyrene*.—1-Formamidobenzo[*c*]cinnoline (1·05 g.), aluminium chloride (61 g.), and sodium chloride (8 g.) were ground together and the mixture heated for 3 hr. at 230—260° and then cooled. Water was added and the mixture was basified with ammonia. The precipitate was filtered off, dried, and extracted repeatedly with benzene. The mixed extracts were concentrated, filtered through alumina, and evaporated to yield a yellow solid (0·7 g.) which was recrystallised from benzene to yield yellow prisms of 4,5,9-*triazapyrene*, m. p. 243—245° (Found: C, 75·8; H, 3·5; N, 20·4. $C_{13}H_7N_3$ requires C, 76·1; H, 3·4; N, 20·5%).

4,5,9-*Triazapyrene Oxide*.—4,5,9-Triazapyrene (0·21 g.) was dissolved in glacial acetic acid (20 ml.) and hydrogen peroxide (80—90% w/w; 4 ml.) was added. The solution, which slowly turned red, was left overnight and then poured into water. The red aqueous solution was extracted with benzene. The extracts were concentrated and chromatographed on alumina. A yellow band was eluted with acetone. The solution yielded a pale yellow solid on evaporation which was crystallised from ethanol to give pale yellow needles (60 mg.) of 4,5,9-*triazapyrene oxide*, m. p. 265—267° (Found: C, 70·5; H, 3·3; N, 20·2. $C_{13}H_7N_3O$ requires C, 70·6; H, 3·2; N, 19·0%).

Spectra.—Ultraviolet spectra were determined with an Optica spectrophotometer, model C.F.4, and infrared spectra with an Infracord model 137.

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[13] J. W. Barton and M. A. Cockett, *J.*, 1962, 2454.