613. 4,10-*Diazapyrenes*

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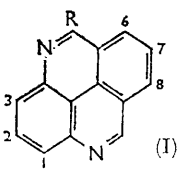
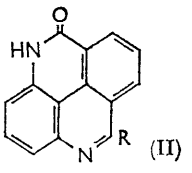
4,10-Diazapyrene and some of its 5-substituted derivatives have been prepared and their oxidation by per-acids examined. Such oxidation resembles that of 4,9-diazapyrene.

We find that the previously unknown 4,10-diazapyrene (I; R = H) and some of its 5-substituted derivatives can conveniently be prepared from 1-aminophenanthridone, which results in good yield from the Schmidt rearrangement [1] of 9-oxofluorene-4-carboxylic acid, and from which can be prepared 1-formamido-, 1-acetamido-, or 1-benzamido-phenanthridone. These amides were easily cyclised in an aluminium chloride and sodium chloride melt, to give the appropriate 4,10-diazapyren-5-one (II). The identity of the


(I)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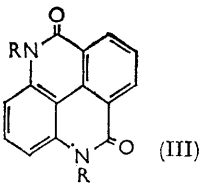
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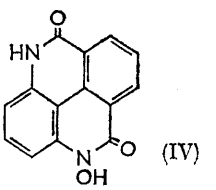
(IV)

products is without doubt. Thus, the ultraviolet absorption curve for (II; R = H) is related to that of 4*H*-4,9-diazapyren-5-one (obtained by the potassium permanganate oxidation in acid of 4,9-diazapyrene [2]) as were the corresponding curves for the 9-substituted compounds (II; R = Me or Ph).

The 1-acylaminophenanthridones failed to cyclise with either phosphorus oxychloride in boiling nitrobenzene or with polyphosphoric acid. The amides (II; R = H, Me, or Ph) were converted into the corresponding 4,10-diazapyrenes by reduction with lithium aluminium hydride. Di- or tetra-hydro-derivatives were never isolated. The 4,10-diazapyrenes prepared had ultraviolet curves nearly identical with those of 4,9-diazapyrene [3] and pyrene.[4]

The per-acid oxidation of these 4,10-diazapyrenes poses an interesting comparison with

[1] A. G. Caldwell and L. P. Walls, *J.*, 1952, 2156.
[2] M. Gawlak and R. F. Robbins, *J.*, 1964, 5135. (The ε values given for 4*H*-4,10- and -4,9-diazapyren-5-one in this Paper are incorrect.)
[3] G. M. Badger and W. F. H. Sasse, *J.*, 1957, 4.
[4] R. A. Friedel and M. Orchin, " Ultraviolet Spectra of Aromatic Compounds," Wiley, New York, 1951.

some 4,9-diazapyrenes. Whilst 5,10-disubstituted 4,9-diazapyrenes give, with peracetic or perphthalic acid, the corresponding di-*N*-oxides, 4,9-diazapyrene gives either a mono- or a di-hydroxamic acid depending on the quantity of per-acid used.[2,5] Not unexpectedly, when 4,10-diazapyrene (I; R = H) was treated with an excess of peracetic or perphthalic acid the dihydroxamic acid (III; R = OH) was obtained. Evidence for this structure rests on the elemental analysis, alkali solubility, characteristic [5] colour reactions, and typical absorptions in the infrared. Furthermore, reduction of this di-hydroxamic acid with iron and dilute hydrochloric acid gave the expected 4,10-dihydro-4,10-diazapyrene-5,9-dione (III; R = H). This amide was also prepared by the chromic acid oxidation of 9-methyl-4*H*-4,10-diazapyren-5-one (II; R = Me).

Attempts to prepare the di-*N*-oxide of 4,10-diazapyrene by treatment with 2 moles of perphthalic acid gave the di-hydroxamic acid (III; R = OH) although in appropriately diminished yield. A mono-hydroxamic acid or a mono-*N*-oxide could not be obtained. *N*-Oxides were not obtained from 5-methyl- or 5-phenyl-4,10-diazapyrene. The amides (II; R = Me or Ph) did not give *N*-oxides either. The latter failed to react even under the most vigorous conditions with peracetic acid. The diamide (III; R = H) also does not react with hot peracetic acid, although the amide (II; R = H) gave the hydroxamic acid (IV).

It seems clear that hydroxamic acid formation in the reactions described does not involve the further oxidation of an intermediate amide. It also appears doubtful that *N*-oxides are intermediates. The peracid oxidation of *N*-oxides to give hydroxamic acids is unusual. We therefore suggest that hydroxamic acid formation depends on an initial attack by the per-acid on the " anil like " 4,5- or 9,10-bonds of a 4,10-diazapyrene. The resulting oxaziridine could then undergo further oxidation and rearrangement of the *N*-oxide to give the required product. An analogous mechanism [2] has been suggested for hydroxamic acid formation from 4,9-diazapyrene.

It is perhaps significant that peracetic acid oxidation of 5-methyl- or 5-phenyl-4,10-diazapyrene gives the corresponding amides (II; R = Me or Ph). If, as supposed, an intermediate oxaziridine were involved, subsequent rearrangement to an amide would not be surprising. 3-(*p*-Nitrophenyl)-2-phenyloxaziridine, for example, readily rearranges on ultraviolet irradiation to 4-nitrobenzanilide, which is also obtained when the preparation of the oxaziridine is attempted by the peracetic acid oxidation of *N*-4-nitrobenzylideneaniline.[6]

Attempted bromination of 4,10-diazapyrene always gave unchanged starting material. Nitration was also attempted in both concentrated sulphuric acid (with potassium nitrate at 100°) and in acetic anhydride (with fuming nitric acid). Even in the solution of lower acidity, where some unprotonated substrate may exist, no reaction takes place. With 4,9-diazapyrene there is some evidence that in an acetic anhydride and fuming nitric acid solution nitration occurs slightly although it is accompanied by oxidation.[7]

Experimental

Ultraviolet spectra were measured, unless otherwise stated, in absolute ethanol on a Uvispec apparatus, and infrared spectra for Nujol mulls with a Perkin-Elmer Infracord spectrophotometer.

1-*Formamidophenanthridone*.—The *product* (14 g., 88%), m. p. >350°, separated, after 6 hours' boiling, from a solution of 1-aminophenanthridone [1] (14 g.) and 99% formic acid (150 ml.). After drying, this material was used in subsequent experiments. Its insolubility in organic solvents prevented the preparation of good analytical specimens, and it decomposed when sublimation was attempted (330°/0·005 mm.).

1-*Acetamidophenanthridone*.—A solution of 1-aminophenanthridone (15 g.) in glacial acetic

[5] R. F. Robbins, *J.*, 1960, 2553.
[6] J. S. Splitter and M. Calvin, *J. Org. Chem.*, 1958, **23**, 651.
[7] M. Gawlak and R. F. Robbins, unpublished observation.

acid (25 ml.) and acetic anhydride (100 ml.) was boiled for 5 hr. and poured into water (1 l.). Crystallisation of the resulting precipitate from ethanol gave the *product* (14·2 g., 79%) as needles, m. p. 217° (Found: C, 71·0; H, 4·8; N, 10·9. $C_{15}H_{12}N_2O_2$ requires C, 71·4; H, 4·8; N, 11·1%).

1-*Benzamidophenanthridone*.—Benzoyl chloride (6 ml.) was added to a solution of 1-aminophenanthridone (10 g.) in pyridine (50 ml.). After standing overnight the mixture was poured into water, and the resulting precipitate washed, dried, and recrystallised from nitrobenzene, to afford the *product* (12·9 g., 86%), m. p. >330° (Found: C, 76·4; H, 4·4; N, 9·0. $C_{20}H_{14}N_2O_2$ requires C, 76·4; H, 4·5; N, 9·1%).

4H-4,10-*Diazapyrene-5-one* (II; R = H).—1-Formamidophenanthridone (3 g.) was added slowly to a melt of anhydrous aluminium chloride (54 g.) and sodium chloride (12 g.) at 100—110°. After 8 hr. at 250° the mixture was poured on to ice, basified with sodium hydroxide, and the resulting solid filtered off, washed, and taken up in warm glacial acetic acid. Filtration of the solution and dilution with water precipitated the *product* (2·6 g., 95%), pale brown needles m. p. 325—326° (nitrobenzene) (Found: C, 76·5; H, 3·9; N, 12·7. $C_{14}H_8N_2O$ requires C, 76·4; H, 3·7; N, 12·7%), $\lambda_{max.}$ 246, 254, 280, 308, 320, 336, 360, 376 mμ (log ε 4·29, 4·27, 4·16, 3·69, 3·69, 3·56, 3·62, 3·72) [cf. 4*H*-4,9-diazapyren-5-one (in MeOH) 243, 253, 273, 306, 317, 344, 358, 376 mμ (log ε 4·53, 4·53, 4·34, 4·00, 3·95, 3·72, 3·97, 4·05)].

9-*Methyl*-4H-4,10-*diazapyren-5-one* (II; R = Me).—(*a*) 1-Acetamidophenanthridone (11·3 g.) was added to a melt of anhydrous aluminium chloride (35 g.) and sodium chloride (15 g.) at 100—110°. After 8 hr. at 250° the mixture was treated as in the previous experiment, to give the *product* (5·4 g., 51·5%), m. p. 329—330°, pale brown needles (from nitrobenzene) (Found: C, 73·8; H, 4·3; N, 11·9. $C_{15}H_{10}N_2O$ requires C, 76·9; H, 4·3; N, 11·8%), $\lambda_{max.}$ 234, 254, 274 mμ (log ε 3·86, 4·31, 4·21), inflexions at 291, 302, 308 mμ (log ε 4·06, 3·86, 3·79), $\lambda_{max.}$ 318, 338, 357, 373 mμ (log ε 3·79, 3·72, 3·72, 3·83).

(*b*) After 24 hr. at 70°, a solution of 5-methyl-4,10-diazapyrene (0·5 g.) in glacial acetic acid (25 ml.) containing 30% hydrogen peroxide (5 ml.) was poured into water. Crystallisation of the resulting precipitate from nitrobenzene gave the *product* (0·41 g., 76%), m. p. 330° undepressed on admixture with a sample from (*a*) (infrared absorption also identical).

9-*Phenyl*-4H-4,10-*diazapyren-5-one* (II; R = Ph).—(*a*) 1-Benzamidophenanthridone (4·0 g.) with aluminium chloride (4·5 g.) and sodium chloride at 250° for 8 hr. gave, after treatment as in (*a*), above, the *product* (II; R = Ph) (2·6 g., 70%) (Found: C, 79·6; H, 4·1; N, 9·7. $C_{20}H_{12}N_2O$ requires C, 81·1; H, 4·1; N, 9·5%), pale brown needles, m. p. 377—378° (from nitrobenzene), $\lambda_{max.}$ 257, 280, 327, 344, 362, 378 mμ (log ε 4·32, 4·33, 4·33, 3·90, 3·88, 3·79, 3·80) with an inflexion at 340 mμ (log ε 3·87).

(*b*) 5-Phenyl-4,10-diazapyrene (0·5 g.), after oxidation with peracetic acid and isolation as in (*b*), above, gave the same product (II; R = Ph) [mixed m. p., and comparison of infrared absorption with the sample prepared in (*a*)].

4,10-*Diazapyrene* (I; R = H).—4*H*-4,10-Diazapyren-5-one (2·3 g.) was extracted (Soxhlet) with boiling tetrahydrofuran into a solution of lithium aluminium hydride (1·2 g.) in the same solvent (150 ml.). After further boiling (10 hr.) the mixture was poured on to ice, made strongly basic with sodium hydroxide, and most of the tetrahydrofuran distilled off. The residue was extracted continuously with ether for about 6 hr. Evaporation of the dried (Na_2SO_4) ether extract and crystallisation of the residue from methanol afforded the *product* (1·91 g., 89%), pale orange needles, m. p. 214° (Found: C, 82·0; H, 4·0; N, 13·8. $C_{14}H_8N_2$ requires C, 82·3; H, 4·0; N, 13·7%), $\lambda_{max.}$ 234, 257, 267, 319, 332 mμ (log ε 4·71, 4·43, 4·36, 4·11, 4·17), inflexion at 304 mμ (log ε 3·92) [cf. 4,9-diazapyrene,[3] 236, 256, 268, 305, 318, 330 mμ (log ε 4·85, 4·32, 4·40, 4·12, 4·18, 4·24) which is similar to pyrene [4] apart from the greater intensity of the group III bands]. 4,10-Diazapyrene gave, as deep red needles, a *picrate*, m. p. 179—180° (Found: C, 55·4; H, 2·6; N, 15·9. $C_{20}H_{11}N_5O_7$ requires C, 55·3; H, 2·2; N, 16·1%), and with methyl iodide it gave an oily product whose further reaction with picric acid in ethanol yielded a *methopicrate*, m. p. 167° (Found: C, 56·0; H, 3·3; N, 15·8. $C_{21}H_{13}N_5O_7$ requires C, 56·4; H, 2·9; N, 15·7%).

5-*Methyl*-4,10-*diazapyrene* (I; R = Me).—9-Methyl-4*H*-4,10-diazapyren-5-one (3 g.) was reduced with lithium aluminium hydride (2 g.) in tetrahydrofuran (150 ml.), as above, to give, from methanol, pale orange needles of the *product* (2·26 g., 81%), m. p. 137—139° (Found: C, 82·3; H, 4·4; N, 12·7. $C_{15}H_{10}N_2$ requires C, 82·5; H, 4·6; N, 12·8%), $\lambda_{max.}$ 235, 267, 304, 332 mμ (log ε 3·67, 3·11, 2·99, 2·85); *picrate*, m. p. 125° (Found: C, 55·9; H, 2·9; N, 15·7. $C_{21}H_{13}N_5O_7$ requires C, 56·4; H, 2·9; N, 15·7%).

5-*Phenyl*-4,10-*diazapyrene* (I; R = Ph).—9-Phenyl-4*H*-4,10-diazapyren-5-one (3 g.), reduced with lithium aluminium hydride in tetrahydrofuran as above, gave the *product* (2·61 g., 92%), pale orange needles, m. p. 161—163° (from ethanol) (Found: C, 85·4; H, 4·9; N, 9·7. $C_{20}H_{12}N_2$ requires C, 85·7; H, 4·3; N, 9·9%), $\lambda_{max.}$ 237, 308, 323, 336 mμ (log ε 4·86, 4·18, 4·26, 4·32), inflexion at 264 mμ (log ε 4·49).

4,10-*Dihydro*-4,10-*diazapyrene*-5,9-*dione* (III; R = H).—9-Methyl-4*H*-4,10-diazapyren-5-one (0·1 g.) was boiled with a solution of potassium dichromate (0·3 g.) in glacial acetic acid (5 ml.) for 2 hr. The mixture was poured into water, and the precipitate washed, dried, and sublimed (330°/0·05 mm.), to give the *product* (0·08 g., 77%), m. p. 330° (Found: C, 71·8; H, 3·7; N, 11·6. $C_{14}H_8N_2O_2$ requires C, 71·2; H, 3·4; N, 11·9%). This product was also (infrared spectra indentical) obtained (26 or 46% yield, respectively) from the reduction of 4,10-dihydroxy- (0·1 g.) (3 hr.) or 10-hydroxy-4*H*-4,10-diazapyrene-5,9-dione (0·1 g.) (6 hr.) with iron powder (0·5 g.) in glacial acetic acid (5 ml.) at 100°. Excess iron was removed by dissolution in dilute sulphuric acid and the insoluble product filtered off.

4,10-*Dihydroxy*-4,10-*diazapyrene*-5,9-*dione* (III; R = OH).—After 24 hr. at 70°, a solution of 4,10-diazapyrene (0·1 g.) in glacial acetic acid (10 ml.) containing 30% hydrogen peroxide (2 ml.) deposited a pale brown solid which gave, after crystallisation from nitrobenzene, the *product* (0·08 g., 63%), m. p. >330° (Found: C, 62·8; H, 3·3; N, 10·7. $C_{14}H_8N_2O_4$ requires C, 62·7; H, 3·0; N, 10·5%). Monoperphthalic acid (either 2 or 4 mol.) in ether gave, with 4,10-diazapyrene in chloroform, the same product (infrared spectra).

10-*Hydroxy*-4H-4,10-*diazapyrene*-5,9-*dione* (IV).—4*H*-4,10-Diazapyren-5-one (0·5 g.) in glacial acetic acid (20 ml.) containing 30% hydrogen peroxide (2 ml.), after 24 hr. at 70°, deposited a brown solid which gave, from nitrobenzene, the *product* (0·44 g., 77%), m. p. >330° (Found: C, 66·9; H, 3·6; N, 11·1. $C_{14}H_8N_2O_3$ requires C, 66·7; H, 3·2; N, 11·1%).

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