# Heteropentalenes.    On    5H-Pyrazolo[1',2':1,2]-1,2,3-triazolo[5,4-a]-phenazinyliumide

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Some properties of the heteropentalenes 5H-pyrazolo[1',2':1,2]-1,2,3-triazolo[5,4-a]phenazinyliumide (1) and 1,3-dimethyl-5H-pyrazolo[1',2':1,2]-1,2,3-triazolo[5,4-a]phenazinyliumide (2) are discussed. The u.v. absorption spectra of the free and of the protonated form are reported.   Catalytic hydrogenation at room temperature reduces the C-6—C-7 double bond so that the loss of aromaticity is minimized.   Compound (2) is oxidized by peracids at room temperature, with attack at the carbon atom in position 12b (negatively charged in the ' azomethinylide ' structure of this heteropentalene) and formation of a quinone imine.

POLYAZAPENTALENES isosteric with the pentalenyl dianion, which thus obey the Hückel aromaticity rule, form an interesting and relatively unexplored class of heterocyclic compounds.   As with other betaine derivatives these compounds cannot be satisfactorily represented by a single covalent or polar structure, but only as resonance hybrids of many dipolar canonical forms.[1]   As part of a programme aimed at acquiring more insight into the chemistry of some classes of these mesomeric betaines, two such compounds, 5H-pyrazolo[1',2':1,2]-1,2,3-triazolo[5,4-a]phenazinyliumide (1) and its dimethyl derivative (2) have been studied for some time in this laboratory.[2]   These compounds are formed in good yields from nitrene intermediates.   A characteristic reaction of these compounds, i.e. the addition of singlet oxygen, was recently reported.[2b]   The present study is aimed at further determining some chemical properties of these pyrazolo-triazolo-phenazinylium inner salts.

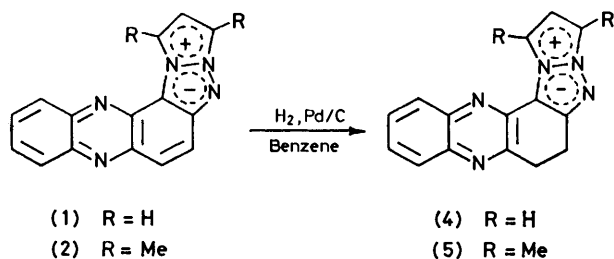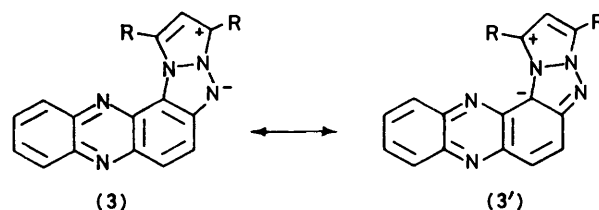## RESULTS AND DISCUSSION

Compounds (1) and (2) consist of 1,3a,6a-triazapentalene nucleus condensed with the phenazine ring, which gives to these derivatives outstanding stability.   In fact, while simple derivatives of the parent 1,3a,6a-triazapentalene are unstable and easily oxidized by atmospheric oxygen,[3] compounds (1) and (2) are crystalline high-



(1)   R = H
(2)   R = Me

(4)   R = H
(5)   R = Me

SCHEME 1

melting solids which melt unchanged and can be handled in air.   Their strongly coloured solutions are stable to the light, provided that oxygen is excluded.   The absorption spectra undergo no marked shift in going from apolar to polar solvents, such as chloroform, alcohols, or acetic acid, only experiencing a change in

shape [e.g. in cyclohexane $\lambda_{max.}$ 552 nm (log $\varepsilon$ 3.95) and 597 (3.96); in chloroform 567 (3.92)].   Apparently, no protonation takes place in pure acetic acid.   However, a complete change is observed in chloroform solution by making it 0.1M in trifluoroacetic acid, showing that complete protonation has occurred [$\lambda_{max.}$ 441 nm (log $\varepsilon$ 3.75) and 757 (3.74)].

Apparently, protonation at different sites takes place concurrently, as the n.m.r. spectra under these conditions show broad signals.   The same absorption spectrum is observed in aqueous solutions in the presence of mineral acids.   These solutions are stable to prolonged refluxing.

Compounds (1) and (2), as with similar heteropentalenes, can be represented as mesomeric hybrids of different dipolar structures, among which the azomethinimine (3) and the azomethinylide (3') can be con-



(3)                                        (3')

sidered.   In fact, several heteropentalenes behave as 1,3-dipoles in relation to dipolar cycloaddition.[1]   If the analogy with simple azomethinimines is valid, catalytic hydrogenation would be expected to cleave the N–N bond, as previously found by Huisgen et al.[4]   In fact, catalytic hydrogenation does take place in very mild conditions (Pd on charcoal, room temperature) to yield in high yield a single product, i.e. (4) from (1) and (5) from (2).

However, the spectroscopic properties of these compounds clearly showed that it was the C-6–C-7 bond which had been reduced.   No trace of 1-pyrazolyl-2-aminophenazine, the expected N–N cleavage product, was observed.   Thus, the triazapentalene moiety remains intact on catalytic hydrogenation, while the reduction takes place in such a way as to minimize the loss of aromaticity in going from the original 22-electron condensed aromatic system to two 10-electron conjugated

systems.* The resistance of a related betaine nucleus to catalytic hydrogenation has been noted in a previous case (2,5-diphenyl-1,2,3-triazolo[4,5-$d$]-1,2,3-triazole).[5] Compounds (1) and (2) undergo singlet oxygen photo-addition, which in the case of (2) occurs as an efficient self-sensitized process.[2b] It was now found that chemical oxidation is also possible, and leads to different results. In fact, compound (2) was completely changed at room

in the i.r. spectrum and a pair of coupled doublets at $\delta$ 7.25 and 9.1 ($J$ 11 Hz). Both elements could be reconciled with a quinone structure and led to the proposal that this product was an $N$-(3,5-dimethylpyrazolyl)-quinone imine.

That this is indeed the case was shown through an examination of the chemical reactivity of (6) (Scheme 2). Thus, refluxing (6) in the presence of $o$-phenylenediamine
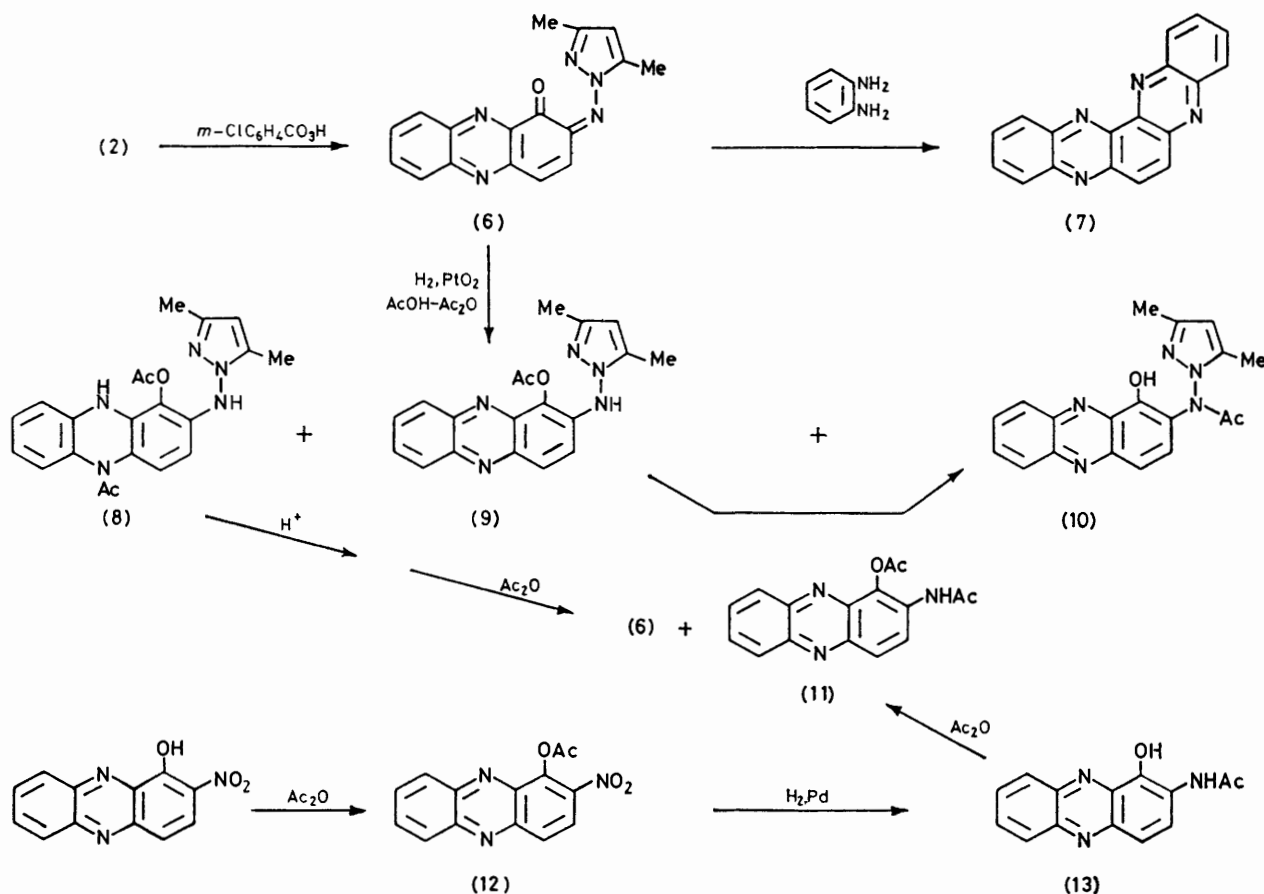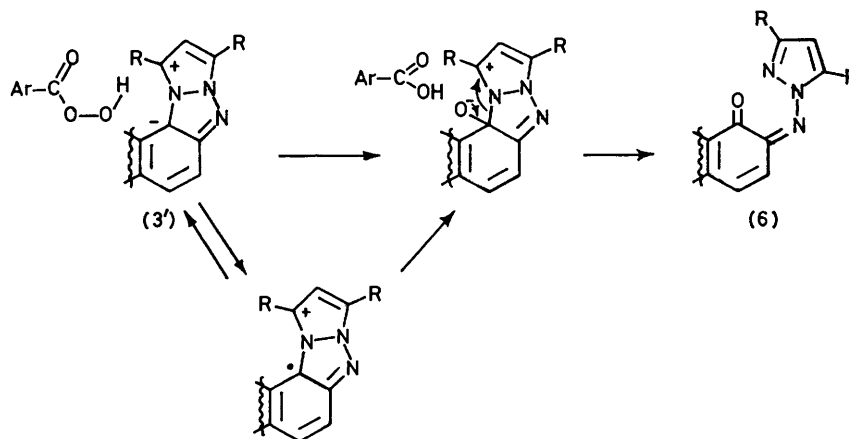


SCHEME 2

temperature with equimolar amounts of $m$-chloroperbenzoic acid in chloroform solution. A red product was first formed, which changed further to a yellow product. Working up of the reaction mixture afforded a crystalline yellow material (6) in 85% yield. This compound was shown by elemental analysis and mass spectrometry to have incorporated one atom of oxygen. Among the most revealing spectroscopic characteristics were an absorption of medium intensity at 1 695 cm⁻¹

* In view of the easy catalytic hydrogenation of phenazine derivatives to $NN'$-dihydrophenazines, it is conceivable that in the case of compounds (1) and (2) also two hydrogen atoms are first added on the nitrogen atoms in positions 7 and 12, and that this intermediate can then either undergo further reduction at the carbon–carbon double bond or transfer the two hydrogen atoms to the carbon–carbon double bond. However, this hypothesis can be discounted since ($i$) only 1 mol hydrogen is adsorbed and ($ii$) $NN'$-dihydrophenazine is not able to reduce compounds (1) and (2).

yielded, together with other products, quinoxalino-[2,3-$a$]phenazine (7), the expected condensation product from an *ortho*-quinone structure. Moreover, catalytic hydrogenation of compound (6) in ethanol gave products difficult to isolate and purify, but tractable products were obtained when the hydrogenation was carried out in acetic acid–acetic anhydride. In such a way one diacetyl and two monoacetyl derivatives were obtained and could be separated by column chromatography. The diacetyl compound, a creamy crystalline solid, was shown by its spectroscopic and chemical properties to be an $N$-acetyl-$NN'$-dihydrophenazine derivative bearing an acetoxy-group. Treatment of this compound with hydrochloric acid detached the acetyl groups, which allowed re-oxygenation of the phenazine ring, and caused a partial detachment of the pyrazolyl group. The reaction mixture was extracted with benzene and

some acetic anhydride was added to the extract. This mixture was separated to yield two products: the starting material (6), which evidently forms by air re-oxidation of the hydrolysis product, and 1-acetoxy-2-acetylaminophenazine (11), identified by direct comparison with an authentic sample, unambiguously prepared from 1-hydroxy-2-nitrophenazine as shown in Scheme 2. Thus, to the diacetyl compound structure

red species, while the formation of the end product (6) requires some time. It is possible that this transient species is the radical cation of (2). A similar hypothesis has been considered by others [6] to explain the change in colour during the oxidation of some diazapentalenes. Whether this species is involved in the formation of (6) or only functions as an unproductive sink remains, at this stage, uncertain.



SCHEME 3

(8) can be attributed, with uncertainty in the position of the acetyl group on the dihydrophenazine ring. As for the two monoacetyl compounds obtained from the hydrogenation of the quinone imine (6), one, compound (9), is an O-acetyl derivative of 2-[(3,5-dimethylpyrazol-1-yl)-amino]-1-hydroxyphenazine; the other, compound (10), is the corresponding N-acetyl derivative. Compound (9) is to a large extent converted into (10) during the working up of the reaction mixture.

Little is known about the peracid oxidation of hetero-pentalenes. The present result contrasts with that reported for the analogous betaine dibenzo-1,2,3-triazolo[1,2-b]-1,2,3-triazole. In that case the attack takes place on a nitrogen and not on a carbon atom and is followed by breaking of the N–N bond with formation of a nitroso-group.[7] However, a reaction somewhat analogous to that of (2) was reported in the case of a hetero-pentalene of different structure, pentaphenylthieno-

TABLE 1

Relevant spectroscopic data on new compounds

| | ¹H N.m.r.[a] | | | | I.r.[b] |
|---|---|---|---|---|---|
| (4) [c] | 6.7 (t) (J 3) (H-2) | | | 3.2—3.4 (m, CH₂CH₂), 7.4—8.1 (m, arom.) | 1 560s, 1 540m |
| | Me groups | | ≳C–H | | |
| (5) [c] | 2.45 (s) | 3.1 (s) | 6.12 (s) | 3.1—3.25 (m, CH₂CH₂), 7.3—7.9 (arom.) | 1 570s, 1 560s, 1 525s |
| (6) [c] | 2.25 (s) | 2.42 (s) | 6 (s) | 7.25 (d, J 11), 9.1 (d), 7.6—8.4 (arom.) | 1 695m |
| (8) [d] | 2.1 (s) | 2.05 (s) | 5.95 (s) | 2.4 (s, OAc), 2.05 (s, NAc), 5.45 (d, J 9) 6.95—7.3 (arom.), 8.45 (s),[e] 9.15 (s) [e] | 3 300s, 1 765s, 1 660s |
| (9) [c] | 2.3 (s) | | 6 (s) | 2.5 (s, OAc), 6.85 (d, J 9), 7.7—8.5 (m, arom.) | 3 250br, 1 770sh, 1 760s |
| (10) [c] | 2.25 (s) | 2.35 (s) | 5.9 (s) | 2.1 (s, NAc), 7.75—8.3 (arom.) | 3 390m, 1 705s |
| (11) [c] | | | | 2.6 (OAc), 2.25 (NHAc), 7.6—8.4 (arom.) | 3 320m, 1 630s, 1 595s |
| (12) [c] | | | | 2.68 (OAc), 7.8—8.5 (arom.) | 1 780s |
| (13) [c] | | | | 2.3 (NHAc), 7.3—8.4 (arom.) | 1 660s |

[a] Chemical shifts in δ, J in Hz. [b] Nujol mull. [c] N.m.r. in CDCl₃. [d] N.m.r. in (CD₃)₂SO. [e] Exchangeable with D₂O.

In conclusion, the mesomeric betaine (2) undergoes peracid oxidation at position 12b, which bears a formal negative charge in the azomethinylide structure (3′). Breaking of the C–N bond ensues to form the quinone imine (6).

About the mechanism of the oxidation, it can be noted that after the peracid has been added, compound (2) is largely transformed (u.v., n.m.r., t.l.c. evidence) into a

[3,4-c]pyrrole. In that case also, a carbon atom is oxidized with breaking of a C–N bond.[8]

In conclusion, the condensation of the triazapentalene and the phenazine moieties in compounds (1) and (2) strongly affects the reactivity of both. Thus, no formation of NN′-dihydrophenazines, normally characteristic of phenazines, is observed in the catalytic hydrogenation. On the other hand, the peracid does not attack either a

TABLE 2

Analytical data for new compounds

| Compound | M.p. | Found (%) | | | Formula | Calculated (%) | | |
|---|---|---|---|---|---|---|---|---|
| | | C | H | N | | C | H | N |
| (4) | 204—206 [a] | 68.8 | 4.3 | 26.4 | $C_{15}H_{11}N_5$ | 68.9 | 4.2 | 26.8 |
| (5) | 186—187 [b] | 71.0 | 5.3 | 23.9 | $C_{17}H_{15}N_5$ | 70.6 | 5.2 | 24.2 |
| (6) | 218 [b] | 67.3 | 4.4 | 23.5 | $C_{17}H_{13}N_5O$ | 67.3 | 4.3 | 23.1 |
| (8) | 188—190 [b] | 64.8 | 5.4 | 17.9 | $C_{21}H_{21}N_5O_3$ | 64.4 | 5.4 | 17.9 |
| (10) | 156—157 [c] | 65.8 | 4.9 | 20.0 | $C_{19}H_{17}N_5O_2$ | 65.7 | 4.9 | 20.2 |
| (11) | 239—240 [b] | 61.4 | 4.9 | 13.8 | $C_{16}H_{13}N_3O_3 \cdot H_2O$ | 61.3 | 4.8 | 13.4 |
| (12) | 156—157 [b] | 59.5 | 3.2 | 15.1 | $C_{14}H_9N_3O_4$ | 59.4 | 3.2 | 14.8 |
| (13) | 221 [b] | 66.2 | 4.5 | 16.5 | $C_{14}H_{11}N_3O_2$ | 66.4 | 4.4 | 16.6 |

[a] From benzene.   [b] From 95% ethanol.   [c] From cyclohexane.

phenazine or triazapentalene nitrogen atom, exclusively reacting at the carbon atom in position 12b.

EXPERIMENTAL

The u.v. and visible spectra were recorded on a Hitachi Perkin-Elmer 200 spectrophotometer, the [1]H n.m.r. spectra on a Perkin-Elmer R-12 instrument, using SiMe$_4$ as internal standard, and the mass spectra on a Du Pont 492-B spectrometer, operating at a source temperature of 190 °C (75 eV).

Compounds (1) and (2) were prepared and purified as previously described.[2a] Commercial (Carlo Erba) pure grade solvents were used after distillation.

*Hydrogenation of Compounds* (1) *and* (2).—Solutions of either (1) or (2) (100 mg) in benzene (50 ml) were hydrogenated at room temperature and atmospheric pressure in the presence of 10% Pd–charcoal (15 mg); 1 mol hydrogen was absorbed and the solution became yellow, with strong green fluorescence. After 5 h the solution was filtered and evaporated, giving a practically quantitative yield of either (4) or (5).

*Chemical Oxidation of Compound* (2).—To a solution of compound (2) (800 mg) in chloroform (200 ml), an equimolar amount of *m*-chloroperbenzoic acid was added. The solution, which turned from blue to red-orange, was stirred for 30 min and then left for 24 h. The solution was then washed with 5% aqueous NaHCO$_3$ and with water, dried, and evaporated, to yield compound (6) (710 mg, 85%), which was recrystallized from ethanol.

*Reaction of Compound* (6) *with* o-*Phenylenediamine*.—A solution of compound (6) (70 mg) and o-phenylenediamine (100 mg) in acetic acid (2 ml) was refluxed for 10 min. The solution was then diluted with water, neutralized with aqueous ammonia, and extracted with ethyl acetate. The organic layer was dried and evaporated and the residue chromatographed on silica gel to yield quinoxalino[2,3-*a*]-phenazine (7) (12 mg) as yellow needles, identical (mixed m.p. and spectroscopic properties) with an authentic sample prepared by the method of Cookson.[9]

*Hydrogenation of Compound* (6).—A suspension of compound (6) (400 mg) in a mixture of acetic acid (20 ml) and acetic anhydride (10 ml) was hydrogenated at room temperature and atmospheric pressure in the presence of PtO$_2$ (40 mg). After 2 h, a colourless solution was obtained, which turned yellow on re-admitting air. Crushed ice (5 g) was added and the mixture was stirred for 30 min, after which solid sodium carbonate was added until pH 5 was reached (*ca.* 40 g). The mixture was extracted with benzene and the organic layer was washed, dried, and evaporated. Chromatography of the residue on silica gel eluting with benzene–ethyl acetate yielded, after a little of the starting

material, compound (10), then a fraction consisting of a mixture of (10) and (9) (by i.r. spectroscopy), then pure (9) and (8). The yields were 11% of product (8), 37% of (9), and 41% of (10).

*Acidic Hydrolysis of Compound* (8).—A suspension of compound (8) (50 mg) in 5M hydrochloric acid (2 ml) was heated at 65 °C for 30 min. The brown solution thus obtained was neutralized with aqueous ammonia and extracted with benzene. T.l.c. of this solution showed the presence of compound (6) and of an easily oxidizable phenolic product. Therefore, acetic anhydride (2 ml) was added to the benzene solution, which turned yellow. After 4 h at room temperature the excess of anhydride was decomposed with water, and the organic layer was separated, dried, and evaporated. Chromatographic separation of the residue on silica gel with benzene–ethyl acetate (1 : 1) yielded compound (6) (10 mg) and compound (11) (8 mg), identical (mixed m.p., spectroscopic properties) with the product obtained *via* an unambiguous synthesis (see below).

*Preparation of Compound* (11).—A suspension of 1-hydroxy-2-nitrophenazine (0.5 g) [10] and a trace of anhydrous zinc chloride in acetic anhydride (5 ml) was heated at 100 °C for 40 min. To the cooled mixture ethanol (5 ml) was added. After 1 h the crystalline yellow precipitate was separated (275 mg). The mother liquor was concentrated yielding a further 160 mg. The combined solids were recrystallized from ethanol yielding 1-acetoxy-2-nitrophenazine (12), m.p. 156—157 °C. A solution of this product (70 mg) in ethanol (50 ml) was hydrogenated at room temperature and ambient pressure in the presence of 10% Pd–charcoal (5 mg). After 2 h the catalyst was filtered off and the yellow solution, which turned orange-red on contact with air, was evaporated, yielding quantitatively 2-acetylamino-1-hydroxyphenazine (13) (the shift of the acetyl group from the hydroxy- to the amino-group is indicated by the shift of the carbonyl absorption in the i.r. spectrum). A suspension of this orange product in benzene (10 ml) and acetic anhydride (1 ml) was heated at 80 °C for 2 h. To the cooled yellow solution thus obtained ethanol (5 ml) was added. After 4 h the solution was concentrated to yield product (11) (60 mg) as a yellow, fluorescent crystalline material.

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