significant factor or contributes equally to the $k_R$'s of all of **1–8**. Then, the radical ion pairs [$BR^{+\cdot}$ $O_2^{-\cdot}$] postulated in the quenching mechanism of **1–5** (eq. 8) can account for the observed products either by collapse to give dioxetanes or endoperoxides[25] which decompose to products (eq. 9), or by H· abstraction en route to BV-like products (eq. 10)[6,22]. The comparatively slow rate ($k_R$) of product formation from **6–8** could thus be ascribed to non-involvement of radical ion pairs or to a less favorable partitioning of the radical ion pair in eqs like 9 and 10.

$$[BR^{+\cdot}\ O_2^{-\cdot}] \rightarrow \text{dioxetanes/endoperoxides} \rightarrow \text{products} \quad (9)$$

$$[BR^{+\cdot}\ O_2^{-\cdot}] \rightarrow [BR-H]\cdot\ O_2H \rightarrow BV + H_2O_2 \quad (10)$$

Other evidence for electron transfer reactions with $^1O_2$ may be found in enamine cleavages which appear to go through an electron-transfer or charge-transfer mechanism involving collapse of an ion-radical pair[26]. 3. The values of $k_Q$ for **1–5** are depressed as the $k_R$ values increase, but ($k_Q + k_R$) is reasonably constant (= 1.8–4.3). The values of $k_R$ and $k_Q$ are fairly invariant for **1–3**, and they are solvent independent, with $k_R < k_Q$. Thus, vinyl groups appear to play no special role, and expected conformational changes (on intramolecular H-bonding[27,28]) due to esterification or protic vs aprotic solvent do not have an appreciable effect on the rates. However, aetiobilirubin (**4**) and the related BR model (**5**) both exhibit substantially enhanced $k_R$ values, $k_R \geq k_Q$. The reasons for the $k_R$, $k_Q$ differences are not clear; however, it seems likely that in the absence of propionic acid (ester) groups, **4** probably assumes a nonintramolecularly H-bonded conformation akin to that of **5**[29]. Thus, whereas the ease of formation of an ion-radical pair intermediate (eq. 8) probably differs little for **1–15**, assuming the same half-wave potentials, the data suggest that the relative ease of chemical reaction (eqs 9 and 10) vs quenching (eq. 8) is conformation dependent.

It would appear that BR is able to quench or react competitively fast with any $^1O_2$ produced in vivo during phototherapy. Since it is almost surely the most reactive local substrate in the environment in which $^1O_2$ is produced[30], BR can control its own photodestruction.

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## 7a-Aza-B-homo[7a,7-d]tetrazole analogues of progesterone and testosterone[1]

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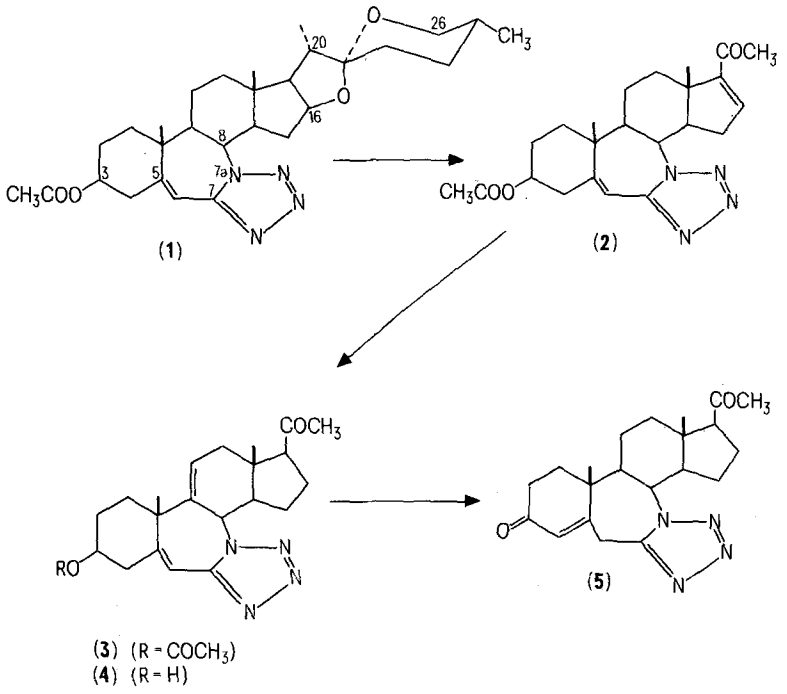
*Summary.* The tetrazole analogues of progesterone and testosterone, namely, 7a-aza-B-homo-4-pregneno[7a,7-d]tetrazole-3,20-dione (**5**) and 3-oxo-7a-aza-B-homo-4-androsteno[7a,7-d]tetrazol-17β-yl acetate (**8**), have been prepared which are worthy of biological testing.

The steroid hormones analogues possessing fused heterocyclic ring system have been found to be of interest. As an extension of our work on steroidal tetrazoles, we have synthesized 7a-aza-B-homo[7a,7-d]tetrazole analogues of progesterone and testosterone.

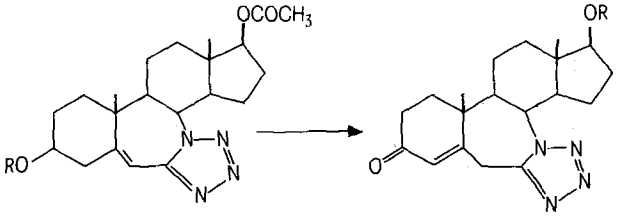
Treatment of (25R)-7-oxo-5-spirosten-3β-yl acetate[2], prepared by tert-butyl chromate oxidation of diosgenin acetate, with hydrazoic acid-boron trifluoride in chloroform[3] gave (25R)-7a-aza-B-homo-5-spirosteno[7a,7-d]tetrazol-3β-yl acetate (**1**): $\nu_{max}$ (KBr) 1724 (ester C=O); 1667 (C=C);




1499, 1466, 1366 (tetrazole bands); 1239 (C–O stretching); $\delta$ 3.46 (2H, m, 26-$CH_2$); 4.50 (3H, m, 8$\beta$-H, 3$\alpha$-H and 16$\alpha$-H); 6.68 (1H, s, 6-CH). The tetrazole (**1**) on Marker degradation gave 20-oxo-7a-aza-B-homo-5,16-pregnadieno[7a,7-d]tetrazol-3$\beta$-yl acetate (**2**): $\nu_{max}$ (KBr) 1736 (ester C=O); 1672 ($\alpha,\beta$-unsaturated C=O); 1600 (conjugated C=C); 1515, 1445, 1370, 1325 (tetrazole bands); 1250 (C–O stretching); $\delta$ 2.30 (3H, s, 21-$CH_3$); 4.76 (2H, broad m, 8$\beta$-H and 3$\alpha$-H); 6.67 (1H, s, 6-CH); 6.84 (1H, t J=3Hz 16-CH). Compound (**2**) on partial hydrogenation[4] over 5% Pd-$BaSO_4$ catalyst[5] gave 20-oxo-7a-aza-B-homo-5-pregneno[7a,7-d]tetrazol-3$\beta$-yl acetate (**3**): $\nu_{max}$ (KBr) 1736 (ester C=O); 1710 (C=O); 1667 (C=C); 1511, 1473, 1443, 1355 (tetrazole bands); 1259 (C–O stretching); $\delta$ 2.20 (3H, s, 21-$CH_3$); 4.27 (1H, m, 8$\beta$-H); 4.76 (1H, m, 3$\alpha$-H); 6.62 (1H, s, 6-CH). Compound (**3**) was hydrolyzed with 6N hydrochloric acid to give hydroxy compound (**4**), which on Oppenauer oxidation using cyclohexanone-toluene system[6] gave 7a-aza-B-homo-4-pregneno[7a,7-d]tetrazole-3,20-dione (**5**): $\lambda_{max}$ (MeOH) 235 nm; $\nu_{max}$ (KBr) 1709 (C=O); 1685 ($\alpha,\beta$-unsaturated C=O); 1616 (conjugated C=C); 1536, 1462, 1439, 1389, 1359 (tetrazole bands); $\delta$ 2.20 (3H, s, 21-$CH_3$); 4.05 (2H, s, 6-$CH_2$); 4.59 (1H, broad m, 8$\beta$-H); 5.90 (1H, s, 4-CH).

7-Oxo-5-androstene-3$\beta$,17$\beta$-diol diacetate[7], prepared by tert-butyl chromate oxidation of 5-androstene-3$\beta$,17$\beta$-diol diacetate, on treatment with hydrazoic acid-boron trifluoride in chloroform[3] gave 7a-aza-B-homo-5-androsteno[7a,7-d]tetrazole-3$\beta$,17$\beta$-diol diacetate (**6**): $\nu_{max}$ (KBr) 1724 (ester C=O); 1667 (C=C); 1504, 1466, 1449, 1370 (tetrazole bands); 1248 (C–O stretching); $\delta$ 4.36 (1H, m, 8$\beta$-H); 4.74 (2H, m, 3$\alpha$-H and 17$\alpha$-H); 6.62 (1H, s, 6-CH). Partial alkaline hydrolysis of (**6**) under mild conditions[8] with potassium bicarbonate gave the monoacetate (**7**). The NMR signals for 8$\beta$-H, 3$\alpha$-H and 17$\alpha$-H appeared as multiplets at $\delta$ 4.28, 3.79 and 4.75, respectively. Oppenauer oxidation of (**7**) using the cyclohexanone-toluene system[6] gave 3-oxo-7a-aza-B-homo-4-androsteno[7a,7-d]tetrazol-17$\beta$-yl acetate (**8**) and the hydrolytic product (**9**) apparently formed during the reaction. Compound (**8**): $\lambda_{max}$ (MeOH) 234 nm; $\nu_{max}$ (KBr) 1736 (ester C=O); 1684 ($\alpha,\beta$-unsaturated C=O); 1616 (conjugated C=C); 1529, 1460, 1429, 1361 (tetrazole bands); 1250 (C–O stretching); $\delta$ 4.05 (2H, s, 6-$CH_2$); 4.73 (2H, m, 8$\beta$-H and 17$\alpha$-H); 5.90 (1H, broad s, 4-CH).

The basis of structural assignments using spectral evidence has been discussed in our earlier publications on steroidal tetrazoles[3,9]. The elemental analyses for the compounds reported here were satisfactory. The analogues (**5**) and (**8**) reported above are worthy of biological testing.

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