diazo-5-methylpyrazole-3-carboxamide and Me_2NH in a similar fashion. *Anal.* ($C_7H_{12}N_6O$) C, H, N.

Ethyl 3-(4-Carbamoylpyrazole-3-yl)-2-triazenoacetate (II).—To a mixt of 40 g of finely powdered glycine·HCl Et ester in 600 ml of EtOAc was added 30 g of Et_3N. The resulting mixt was stirred at room temp for 1 hr. To this was added 20 g of powdered 3-diazopyrazole-4-carboxamide[3] and the mixt was stirred for 24 hr. The solid was collected by filtration and extd repeatedly with hot 50% aq MeOH. The insol solid, which melted at 220–222° dec and possessed $\lambda_{max}^{pH\ 11}$ at 402 nm, has not yet been identified. The filtrate was concd *in vacuo* to yield 9 g of analytically pure II, mp 145°. *Anal.* ($C_5H_{12}N_6O_3 \cdot H_2O$) C, H, N, H_2O.

1-[(4-Carbamoylpyrazol-3-yl)azo]DL-proline (III).—To a mixt of 20 g of finely powdered 3-diazopyrazole-4-carboxamide[3] in 500 ml of MeOH was added 40 g of finely powdered DL-proline. The mixt was stirred at 25° for 18 hr and the solid collected by filtration. It was recrystd from 50% aq MeOH to give 5 g of III, mp 188–189°. *Anal.* ($C_9H_{12}N_6O_3$) C, H, N.

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Steroidal Heterocycles. 14.[1] 1,8a-Epoxy-1,4,4a,5,6,7,8,8a-octahydro-2-hydroxynaphthalene-3-carbonitrile and Related Compounds

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4α,5-Epoxy-3,17β-dihydroxy-5α-androst-2-ene 2-carbonitrile (**9**) and related steroids block the ACTH-induced catabolic and thymolytic responses in castrate male rats.[1] Therefore, it seemed of interest to determine whether related bicyclic compds resembling rings A/B of these steroids would exhibit similar activity. Using known procedures[2-4] indicated in the flow sheet, 2-methylcyclohexanone (**1**) was converted in a series of steps into 1,8a-epoxy-1,4,4a,5,6,7,8,8a-octahydro-4a-methylnaphtho[2,3-*d*]isoxazole (**7**) which was rearranged to **8** with base.

Biological Testing.—Compd **8** showed none of the ACTH-induced catabolic blocking of the corresponding steroid **9** in castrated rats. It did exhibit slight bacteriostatic and fungistatic activities.

Experimental Section

All melting points were taken on a Fisher-Johns melting point apparatus, uncor. Uv spectra were detd in 95% EtOH (Cary 15) and ir in KBr disks (Perkin-Elmer 21). Nmr spectra were measured with (Me_4Si) in $CDCl_3$ (Varian A60). Where analyses are indicated only by symbols of the elements, anal. results obtained for those elements were within ±0.4% of the theor values.

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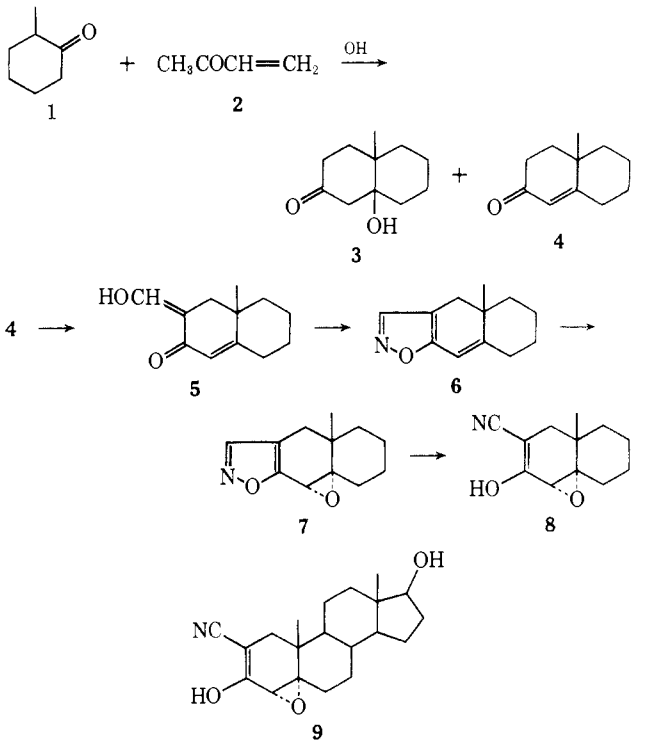

1,8a-Epoxy-1,4,4a,5,6,7,8,8a-octahydro-4a-methylnaphtho[2,3-*d*]isoxazole (**7**).—The distd hydroxymethylene compd **5**[3] gave an isoxazole **6** with H_2NOH,[3] obtd as an amber resin. Crude resin **6** (no attempt was made to purify **6**) (17.5 g) was dissolved in CH_2Cl_2 (300 ml) and added to H_2O_2 (6 ml; 1.3 g/ml) and maleic anhydride (20 g) in CH_2Cl_2 (100 ml) at 0°.[4] The soln was swirled vigorously, and C_5H_5N (5 drops) was added. The soln became turbid immediately as maleic acid pptd and was kept in a refrigerator overnight. Satd Na_2SO_3 soln was added dropwise with stirring until starch–iodide paper no longer darkened. The soln was washed with $NaHCO_3$ soln, dried ($MgSO_4$), filtered, and concd on a steam bath. Faint yellow, cryst material was obtained (8.89 g; 46.8% yield); the rest was dark amber resin. The product was crystd (EtOAc): mp 85–86°; λ_{max} 237 mμ (6850). *Anal.* ($C_{12}H_{15}NO_2$) C, H, N.

1,8a-Epoxy-1,4,4a,5,6,7,8,8a-octahydro-2-hydroxy-8a-methylnaphthalene-3-carbonitrile (**8**).—Isoxazole **7** (19.5 g) was dissolved in THF (200 ml), stirred, and cooled in an ice bath. NaOMe (10.8 g) was added and soon a thick ppt of the Na salt of **8** formed. After 2 hr of stirring, Et_2O (100 ml) was added, and the salt was filtered and rinsed with Et_2O. After most of the Et_2O adhering to the salt had dissipated, it was dissolved in H_2O (200 ml), Na_2HPO_4 (10 g) was added, and the soln was acidified with dil HCl. The oily ppt was extd with Et_2O, dried ($MgSO_4$), and concd on a steam bath to afford 18.5 g (85%) of granular crystals, mp 98–100°. They were recrystd (EtOAc): mp 100–102°; λ_{max} 252 mμ (9400), ir 4.54, 5.81 (weak, medium), 6.16 μ. Nmr also indicated a mixt of keto–enol tautomers.[1] *Anal.* ($C_{12}H_{15}NO_2$) C, H, N.

Synthesis of 2-Methylpteridine Derivatives

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We have previously reported on pyrido[2,3-*d*]pyrimidine derivatives, which are potential pteridine antagonists as well as azalogs of nalidixic acid.[1] A continuing

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