3-Hydroxy-16,17-seco-16-norestra-1,3,5(10)-trien-17-oic Acid (1b).—The hydrogenolysis of the benzyl group of 1.00 g of **10** was accomplished as described in the preparation of **11**. The solid residue was crystallized from Me_2CO–*n*-C_6H_{14} to give 0.63 g (84%) of **1b**, mp 195–198° (evac tube). The analytical sample was obtained from C_6H_6 as thick needles, mp 198.5–200.5° (evac tube), $[\alpha]D$ +69° (EtOH). *Anal.* ($C_{17}H_{22}O_3$) C, H.

Doisynolic Acid (1a).—Doisynolic acid was prepared by the method of Heer and Miescher.[4] From 4.0 g of estrone there was obtained, after four crystallizations from MeOH–H_2O and one from Me_2CO–*n*-C_6H_{14}, 0.179 g of colorless needles, mp 198.5–200° (evac tube), $[\alpha]D$ +105° (*c* 0.470, EtOH) [lit.[4] mp 199–200°, $[\alpha]D$ +102° (*c* 0.475, in EtOH)].

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New Compounds

An Aziridinone Derived from 1-Aminoadamantane

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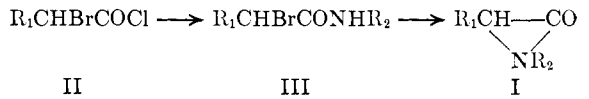
Although the physiological properties of aziridines have been extensively investigated, especially in connection with the nitrogen mustards, there is no report in the literature regarding the biological properties of aziridinones. We report here the preparation of an aziridinone (I), which is a derivative of 1-aminoadamantane, a compound in which there has been a considerable pharmacological interest since its antiviral activity was discovered.[2]



R_1 = *t*-Bu
R_2 = 1-adamantyl ($C_{10}H_{15}$)

Experimental Section[3]

N-(1-Adamantyl)-2-bromo-3,3-dimethylbutyramide (III).—A solution of 1.00 g (8.6 mmoles) of 3,3-dimethylbutyric acid in $SOCl_2$ (1.0 ml) was refluxed for 30 min and excess $SOCl_2$ was removed under reduced pressure at 30°. The acid chloride was dissolved in 2.3 ml of CCl_4 and refluxed with Br_2 (0.53 ml, 9.6 mmoles) for 2.5 hr. The resulting bromo acid chloride was treated gradually with an ice-cold solution of 1.31 g (8.6 mmoles) of 1-aminoadamantane and 1.14 g (11 mmoles) of Et_3N in 60 ml of CH_2Cl_2. The reaction mixture was then treated with H_2O, extracted with CH_2Cl_2, and the combined CH_2Cl_2 layers were washed (5% HCl, 5% NaOH, H_2O, saturated NaCl solution) and dried (Na_2SO_4). The solvent was removed *in vacuo* to give crude III, which was recrystallized from heptane to furnish 2.30 g (82% over-all) of crystals, mp 182–183°. *Anal.* ($C_{16}H_{26}BrNO$) C, H, Br, N.

1-(1-Adamantyl)-3-*t*-butylaziridinone (I).—A solution of 1.00 g (3.1 mmoles) of III in 150 ml of dry Et_2O was stirred with 0.55 g (4.9 mmoles) of KO-*t*-Bu at 0° for 15 min (progress of the reaction was followed by ir spectroscopy). The reaction mixture was filtered through a sintered-glass funnel and the filtrate was removed under reduced pressure at room temperature. The solid residue was recrystallized from heptane to afford 0.51 g (68%) of the aziridinone **I**: mp 82–83°; ir, 1830 cm^{-1}; nmr, τ 7.32 (1 H, s), 7.73–8.42 (15 H, m), 9.02 (9 H, s). *Anal.* Calcd for $C_{16}H_{25}NO$: C, 77.68; H, 10.19; N, 5.66. Found: C, 77.46; H, 10.07; N, 5.55.

(1) Recipient of a Graduate Traineeship from the National Science Foundation.

(2) W. L. Davies, R. R. Grunert, R. F. Haff, J. W. McGahen, E. M. Neumayer, M. Paulshock, J. C. Watts, T. R. Wood, E. C. Hermann, and C. E. Hoffmann, *Science*, **144**, 862 (1964).

(3) Melting points were taken on a Mel-Temp apparatus and are uncorrected. Ir spectra were obtained in $CHCl_3$ on a Perkin-Elmer spectrophotometer, Model 337, and nmr spectra were recorded in CCl_4 as solvent on a Varian A-60 instrument (TMS as internal standard). Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Some Aromatic Fluorine Compounds

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Fluorination of carcinogenic aminoazo dyes greatly enhances the activity of these compounds except when the sites involved in carcinogenesis are blocked by substitution with the halogen.[1,2] As these sites are on the diamine ring, various difluoroanilines are required for synthesis of the dyes. This communication reports some observations and new compounds of interest which have arisen during attempts to prepare 2,3-difluoroaniline.

Experimental Section[3]

2-Chloro-3-fluoronitrobenzene.—2,3-Dinitroaniline[4] (162 g) was suspended in HCl (5.5 *N*, 490 ml) and a solution of $NaNO_2$ (100 g) in H_2O (120 ml) was added slowly with constant stirring, the temperature being maintained below 0° by the addition of solid CO_2 to the mixture. The mixture was stirred for a further 30 min and then a slight excess (204 g) of solid sodium fluoroborate was added slowly with constant stirring. After a further 30 min, the precipitate was filtered off under vacuum, washed with a small volume of chilled saturated sodium fluoroborate solution, and allowed to dry in the dark. The product, **2-chloro-3-nitrobenzenediazonium fluoroborate,** was a bright yellow solid (193 g, 80%) which darkened upon exposure to light. The diazonium salt was dried further in a desiccator (NaOH, silica gel) and then decomposed by intimately mixing small portions (10 g) with washed, dried sand (20 g) in a 500 ml round-bottomed flask fitted with a condenser and heating carefully in an oil bath.

(1) J. A. Miller, E. C. Miller, and G. C. Finger, *Cancer Res.*, **13**, 93 (1953).

(2) J. A. Miller, E. C. Miller, and G. C. Finger, *ibid.*, **17**, 387 (1957).

(3) Melting points are corrected and were determined in a capillary tube; boiling points are uncorrected. Analyses were performed by the CSIRO Australian Microanalytical Service.

(4) K. H. Pausacker and J. G. Scroggie, *J. Chem. Soc.*, 1897 (1955).