mole) of benzyl β-chloroethyl ether.[8] After stirring and heating the mixture on the steam bath for 19 hr., the dimethylformamide was removed by distillation under reduced pressure, and the cooled residue was treated with 250 ml. of cold water. Insoluble oil was taken up in ether and dried over anhydrous magnesium sulfate. Filtration and removal of the ether by distillation gave a thick oil which, on fractionation, gave 29 g. (30%) of IV, b.p. 208–213° (0.3 mm.), n_D^{25} 1.5920, m.p. 64–66° (from hexane), $\lambda_{max}^{CHCl_3}$ 5.55 μ (> C=O).

Anal. Calcd. for $C_{23}H_{20}O_3$: C, 80.21; H, 5.85; O, 13.94. Found: C, 80.09; H, 5.91; O, 14.00.

2-(o-Hydroxyphenyl)-2-phenyl-4-hydroxybutyric acid γ-lactone (IIIa). A solution of 5 g. (0.0145 mole) of IV in 100 ml. of ethanol was hydrogenated at 55–60° and 40 lb. of pressure for 16 hr. using 2.5 g. of 5% palladium-charcoal catalyst. After recovery of the catalyst by filtration, the ethanol was removed using a rotating evaporator under reduced pressure. The solid residue (3.6 g., 97%), m.p. 146–151°, was recrystallized twice from benzene to give 2.8 g. (76%) of pure IIIa, m.p. 159–161°, identical (mixed melting point and infrared spectrum) with the material obtained from Ia[1]; $\lambda_{max}^{CHCl_3}$ (μ) 2.78(w), 3.0(w) (broad), 5.65(m) (shoulder), 5.74(s), 6.21(w), 6.33(w), 6.76(m), 7.29(m).

Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55; O, 18.88. Found: C, 75.72; H, 5.47; O, 18.53.

Refluxing 2.3 g. (0.009 mole) of IIIa for 18 hr. with a mixture of 10 ml. of 48% hydrobromic acid and 25 ml. of glacial acetic acid gave a quantitative yield of 3-(β-bromoethyl)-3-phenyl-2-benzofuranone (Ia) identified by mixed melting point and infrared spectral comparison with the authentic material.[1]

3-(γ-Hydroxypropyl)-3-phenyl-2-benzofuranone (IIb). The fraction (5.3 g.), b.p. 200–201° (1.5 mm.), obtained as an appreciable by-product in the preparation[1] of ethyl 5-phenyl 2,3,4,5-tetrahydro-1-benzoxepin-5-carboxylate by treatment of 3-(γ-chloropropyl)-3-phenyl-2-benzofuranone with sodium ethoxide, was dissolved in 10 ml. of a 10% solution of potassium hydroxide in methanol. After standing overnight, a solid potassium salt (5.3 g.) crystallized. It was collected by filtration and dried. This was dissolved in a little water and acidified with dilute hydrochloric acid. The precipitated oil (3.5 g.) quickly solidified and was collected at the filter, washed with chloroform, and dried, m.p. 113–114° (gas evolution). The infrared spectrum, λ_{max}^{Nujol} 5.93 μ (> C=O), and analysis were consistent with the structure, 2-(o-hydroxyphenyl)-2-phenyl-5-hydroxyvaleric acid.

Anal. Calcd. for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34; O, 22.35. Found: C, 71.88; H, 6.35; O, 21.79.

Attempts to recrystallize this acid were unsuccessful. After standing in chloroform for several days it reverted spontaneously to the chloroform-soluble benzofuranone IIb, $\lambda_{max}^{CHCl_3}$ 5.54 μ (>C=O). Pure IIb was obtained by removal of the chloroform by evaporation and distillation of the residue, b.p. 193–195° (1 mm.), n_D^{25} 1.5830; $\lambda_{max}^{CHCl_3}$ (μ) 2.74(w), 3.30(w), 3.38(w), 3.45(w), 5.54(s), 6.17(w), 6.24(w), 6.68(w), 6.77(m), 6.83(s), 6.91(w).

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01; O, 17.89. Found: C, 76.33; H, 6.13; O, 18.03.

Refluxing 2 g. (0.0075 mole) of the benzofuranone IIb with hydrobromic acid in acetic acid as described above for the lactone IIa gave 1.9 g. (77%) of 3-(γ-bromopropyl)-3-phenyl-2-benzofuranone (Ib), m.p. 92–94°, identified by infrared spectrum and mixed melting point with an authentic specimen.[1]

Spectra. The infrared spectra were determined using a Perkin-Elmer Model 137-G Grating Infracord, and the ultraviolet spectra using a 1-cm. cell in a Cary Model 11 recording spectrophotometer.

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Ultraviolet Spectra of Unsaturated Cyclic Nitriles

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A study of the ultraviolet spectra of a number of unsaturated aliphatic nitriles[1] led to the following rules as regards the effects of substituents on wave length: unsubstituted, 203; α- or β-monosubstituted, 205 ± 3; α,β- or β,β-disubstituted, 210 ± 3; and α,β,β-trisubstituted, 216 ± 2 mμ. Only one cyclic nitrile (1-cyanocyclohexene) was included in this study, and the ultraviolet spectra of a number of unsaturated cyclic nitriles are now considered (see Table I). These include present determinations and data taken from the literature.[2]

The α,β-disubstituted six-membered ring nitriles had their maxima at *ca.* 210 mμ, the same as that of the cyclic compounds.[1] The second maximum reported for 1-cyano-4-isopropylcyclohexene (at 271 mμ)[2e] was not observed in the other cases and may be due to an impurity (the intensity of the maximum at 212 mμ was also significantly lower). A band has been detected at 270 mμ in nitriles, but its intensity was extremely low ($A_m < 10^{-3}$).[3]

α,β-Disubstituted five-membered ring nitriles, however, had their maximum at 215–220 mμ. Similar bathochromic shifts have been noted in other five-membered endocyclic compounds[2a,4] and have been attributed[2a] to ring strain. The variation in the wave length of the maximum of these nitriles reflects the varying strain in their rings. 1-Cyano-

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TABLE I

Ultraviolet Spectra of Unsaturated Nitriles

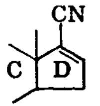
Substitution	Nitrile	λ_{max}	A_m[a]
α,β-Six-ring	1-Cyanocyclohexene	212	11,400[b,c]
	1-Cyano-6-methylcyclohexene	210	9,500[d]
	1-Cyano-4-isopropylcyclohexene	212 271	8,900[e] 102
α,β-Five-ring	1-Cyanocyclopentene	216	10,150[b,f]
	3β-Acetoxy-17-cyano-5,16-androstadiene	218	9,200[b,g]
	3β-Acetoxy-17-cyano-5α,6α-epoxy-16-androstene	219	9,300[b]
	3β-Acetoxy-16-cyano-5,15-androstadiene	225	12,500[h]
	3β-Acetoxy-16-cyano-5,16-androstadiene	220	10,000[h]
	1-Cyanocycloheptene	216	10,250[b,i]
β,β-Six-ring	Cyclohexylideneacetonitrile	216	13,150[b,j]
β,β-Five-ring	Cyclopentylideneacetonitrile	220	12,800[b]
α,β,β-Five-ring	20-Cyano-3β,21-diacetoxy-5,17-pregnadiene	224	10,500[k]
	21-Acetoxy-20-cyano-3,3-dimethoxy-17-pregnene-11-one	222.5	14,800[l]
	21-Acetoxy-20-cyano-3,3-diethoxy-17-pregnene-11-one	222.5	14,500[l]
	20-Cyano-3,3-dimethoxy-17-pregnene-11-one	222.5	14,700[l]
	20-Cyano-11β,21-dihydroxy-17-pregnene-3-one	222.5	14,150[l]
	20-Cyano-21-hydroxy-17-pregnene-3,11-dione	223	13,700[l]
	21-Acetoxy-20-cyano-11β-hydroxy-17-pregnene-3-one	222.5	14,800[m]
	21-Acetoxy-20-cyano-17-pregnene-3,11-dione	222	14,650[m]

[a] All spectra determined in ethanol solution, unless otherwise stated. Wave lengths in mμ. [b] Present work. [c] Ref. 1 gives 208 (12,500); ref. 2a 212 (11,200); ref. 2b 211 (4200); ref. 2c gives 230 (1600), 261 (60). This last value must be in error. [d] Ref. 2d. [e] Ref. 2e. [f] Ref. 2a gives 217 (9900). [g] Ref. 2f gives 216 (7600). [h] Ref. 2g. [i] Ref. 2a gives 216 (10,500). [j] Ref. 2b gives 217 (13,700). [k] Ref. 2h. [l] Ref. 2i. [m] Ref. 2j.

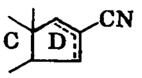
cycloheptene also falls in this group, its ring being likewise strained.[2a]

The β,β-disubstituted six-membered nitrile, cyclohexylideneacetonitrile absorbed at 216 mμ and the corresponding five-membered nitrile, cyclopentylidene-acetonitrile, at 220 mμ (Table I). Both of these values are higher than for acyclic unsaturated nitriles[1] and exocyclic ring compounds generally show bathochromic shifts.[2a]

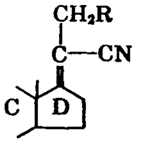
The group of the steroid α,β,β-trisubstituted unsaturated nitriles (I–III) absorbed at 222–224 mμ (Table I) for both the endocyclic Δ^{16}-17-nitriles (I) and the Δ^{15}- and Δ^{16}-16-nitriles (II) as well as the exocyclic Δ^{17}-20-nitriles (III). These values are again displaced to longer wave length with respect to the acyclic analogues and demonstrate the effect of both endo- and exocyclic strain in a five-membered ring.



I



II



III

The results for unsaturated ring nitriles are very similar to those for α,β-unsaturated acids and esters (α- or β-, 208; α,β- or β,β-, 217; α,β,β-, 225 mμ).[4] α,β-Unsaturated aldehydes and ketones absorb at higher wave lengths (at *ca.* 230 mμ)[2a] and this is in agreement[5] with the suggestion that the nitrile group has a greater resonance effect than the aldehyde grouping.

EXPERIMENTAL

Compounds. 1-Cyanocyclopentene and 1-cyanocycloheptene were prepared from the corresponding ketones *via* their cyanohydrins.[6] Cyclopentylideneacetonitrile and cyclohexylideneacetonitrile were prepared by isomerization[7] of 1-cyclopentenyl- and 1-cyclohexenylacetonitrile.[8] 3β-Acetoxy-17-cyano-5,16-androstadiene and 3β-acetoxy-17-cyano-5α,-6α-epoxy-16-androstene were analytical samples.[9]

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N,N-Diphenylthiocarbamates as Derivatives of Mercaptans[1]

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As part of another program it was necessary to obtain solid derivatives of several mercaptide ions

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