TABLE I

Ultraviolet Spectra of Unsaturated Nitriles

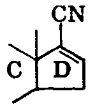
Substitution	Nitrile	λ_{max}	A_m[a]
α,β-Six-ring	1-Cyanocyclohexene	212	11,400[b,c]
	1-Cyano-6-methylcyclohexene	210	9,500[d]
	1-Cyano-4-isopropylcyclohexene	212 271	8,900[e] 102
α,β-Five-ring	1-Cyanocyclopentene	216	10,150[b,f]
	3β-Acetoxy-17-cyano-5,16-androstadiene	218	9,200[b,g]
	3β-Acetoxy-17-cyano-5α,6α-epoxy-16-androstene	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.

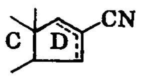
cycloheptene also falls in this group, its ring being likewise strained.[2a]

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]

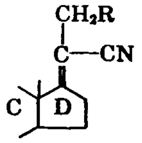
The group of the steroid α,β,β-trisubstituted unsaturated nitriles (I–III) absorbed at 222–224 mμ (Table I) for both the endocyclic Δ^{16}-17-nitriles



I



II



III

(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.

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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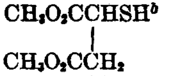
(2) Tennessee Eastman Corp. Fellow, 1959–60. National Science Foundation Cooperative Fellow, 1960–61.

(3) Undergraduate research student.

TABLE I

N,*N*-DIPHENYLTHIOCARBAMATE DERIVATIVES OF MERCAPTANS

Mercaptan	M.P.[a] (±1°)	Calcd. for	Calcd., %		Found, %	
			C	H	C	H
C_2H_5SH	(108)[c]					
i-C_3H_7SH	124.0	$C_{16}H_{17}NOS$	70.85	6.32	70.75	6.14
n-C_4H_9SH	60.0	$C_{17}H_{19}NOS$	71.58	6.71	71.59	6.70
n-$C_6H_{13}SH$	48.0	$C_{19}H_{23}NOS$	72.80	7.40	72.52	7.41
n-$C_7H_{15}SH$	50.0	$C_{20}H_{25}NOS$	73.35	7.70	73.63	7.59
p-$CH_3OC_6H_4CH_2SH$	131.4	$C_{21}H_{19}NO_2S$	72.17	5.48	72.17	5.51
$C_6H_5CH_2SH$	124 (125)[c]					
$HOCH_2CH_2SH$	84.8	$C_{15}H_{15}NO_2S$	65.97	5.53	66.02	5.66
C_6H_5SH	125	$C_{19}H_{15}NOS$	74.72	4.95	74.87	4.94
o-$CH_3C_6H_4SH$	94.5	$C_{20}H_{17}NOS$	75.20	5.36	75.44	5.40
m-$CH_3C_6H_4SH$	121.5	$C_{20}H_{17}NOS$	75.20	5.36	75.25	5.48
p-$CH_3C_6H_4SH$	174.2 (180–182)[c]	$C_{20}H_{17}NOS$	75.20	5.36	75.22	5.44
o-$NH_2C_6H_4SH$	145.3	$C_{19}H_{16}N_2OS$	71.23	5.04	71.53	5.32
$CH_3O_2CCH_2SH$	116.5	$C_{16}H_{15}NO_3S$	63.76	5.02	64.14	5.23
$CH_3O_2CCH_2CH_2SH$[b]	96.5	$C_{17}H_{17}NO_3S$	64.74	5.43	64.80	5.33
$C_2H_5O_2CCH_2SH$[b]	101.6	$C_{17}H_{17}NO_3S$	64.73	5.43	64.50	5.43
 CH_3O_2CCHSH[b] $CH_3O_2CCH_2$	101.5	$C_{19}H_{19}NO_5S$	61.11	5.13	61.02	5.14
$C_6H_5COCH_2SH$	136.2	$C_{21}H_{17}NO_2S$	72.60	4.93	72.91	5.01

[a] All melting points (capillary) are corrected. Elemental analysis by Micro-Tech Laboratories, Skokie, Ill. [b] Generous samples of β-mercaptopropionic acid and σ-mercaptosuccinic acid were kindly supplied by Evans Chemetics, Inc., New York, N. Y. [c] R. L. Evans and W. M. Dehn, *J. Am. Chem. Soc.*, 52, 3645 (1930).

in the presence of cyanide ion and alcohol. Although a number of alkylating agents and unsaturated compounds have been employed as mercaptan reagents, very few were suitable under the necessary conditions. The suggested use[4] of *N*,*N*-diphenylcarbamyl chloride (I) as a mercaptan acylating agent prompted a study of this substance. Mercaptides were found to react readily with I in the presence of cyanide ion or alcoholates and, in fact, afforded such easily purified adducts that use as a general characterizing agent for mercaptans seemed appropriate. The derivatives obtained (80–95%) are listed in Table I.

EXPERIMENTAL

The mercaptans used were obtained commercially or were prepared by known procedures. The *N*,*N*-diphenylcarbamyl chloride was obtained from Eastman Organic Chemicals.

Preparation of N,N-diphenylthiocarbamate derivatives. A solution containing 0.23 g. (0.01 g.-atom) of sodium in 30 ml. of alcohol was treated with 0.01 mole of mercaptan. The solution of mercaptide was then added to a solution of 2.31 g. (0.01 mole) of *N*,*N*-diphenylcarbamyl chloride in 20 ml. of alcohol. The solution was warmed on a steam bath for 5 min., the precipitated salt filtered, and the derivative allowed to crystallize. Cooling was sometimes necessary to induce crystallization. Recrystallization was easily effected from alcohol. In general, the melting point was not raised after one recrystallization.

The only mercaptans studied which did not afford derivatives in high yield were *p*-nitrobenzyl mercaptan, β-mercaptopropionic acid, and α-mercaptosuccinic acid.

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Some Aminoethylpiperidines and -pyridines

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Several previously unreported compounds were synthesized during preparation of a series of aminoethylpiperidines.

Addition of amines[1] or ammonia[1c] to 2- or 4-vinylpyridine gave aminoethylpyridines which were catalytically reduced to piperidines.

An attempt to pyridylethylate ammonia as described by Magnus and Levine[1c] gave principally bis[2-(2-pyridyl)ethyl]amine rather than 2-(2-aminoethyl)pyridine. The latter could be made by variation of the conditions of this reaction.

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