ethanol) gave a peak of 280 mμ typical for indoles and it did not change after acidification. The nmr spectrum contained five peaks and was interpreted after integration as representative of eight aromatic hydrogens (τ 1.0–3.0), two pyrrole N-*H*, two N-N*H*$_2$, four C*H*$_2$, and two indole-2 hydrogens.

2-Hydrazino-8-quinolinol and Derivatives[1]

TERRY RUDOLPH, F. PRZYSTAL, AND J. P. PHILLIPS

Department of Chemistry, University of Louisville, Louisville, Kentucky

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Hydrazones of carbonyl compounds and 2-hydrazino- and 2-(1-methylhydrazino)-8-quinolinols were prepared for antitumor tests. Those hydrazones from formyl-8-quinolinols might be of further interest as bifunctional chelating agents.[2,3]

Experimental Section[4]

2,8-Quinolinediol[5] was tosylated and chlorinated with PCl$_5$–POCl$_3$ in agreement with the literature,[6] although final hydrolysis with alkali to 2-chloro-8-quinolinol gave a product of substantially higher melting point (83–84°) than reported.

2-Hydrazino-8-quinolinol.—2-Chloro-8-quinolinol (5 g) was refluxed in 20 ml of 40% hydrazine for 4 hr. Solvent was removed under vacuum and 15 ml of water was added to precipitate the product. Recrystallization from 95% ethanol yielded a tan solid, mp 177–178° (81% yield).

Anal. Calcd for $C_9H_9N_3O$: C, 61.70; H, 5.17; N, 23.97. Found: C, 61.87; H, 5.09; N, 23.84.

Although reasonably stable as the solid, the hydrazine in solution decomposed in a few hours. The ultraviolet spectra in various solvents showed λ_{max} [mμ (log ε)]: EtOH, 245 (4.27), 263 (4.46), 280 s (4.04); 0.1 *N* HCl, 240 (4.12), 264 (4.40), 304 (3.87), 340 s (3.52); 0.1 *N* NaOH, 252 (4.36), 274 s (4.02), 330 (3.46), 356 s (3.41). The infrared spectra (KBr) showed bands at 3345, 3330, 1520, 1240, 820, and 738 cm^{-1} (strongest bands).

2-(1-Methylhydrazino)-8-quinolinol.—2-Chloro-8-quinolinol (1 g) and 0.39 g of methylhydrazine in 1-propanol as solvent were refluxed 24 hr. Evaporation of solvent, addition of 50 ml of water, and neutralization with K_2CO_3 precipitated the product, mp 106° after recrystallization from ligroin (80% yield). The ultraviolet spectra showed λ_{max} [mμ (log ε)]: EtOH, 250 s (4.27), 269 (4.52), 351 (3.56); 0.1 *N* HCl, 244 (4.23), 269 (4.48), 312 (3.48), 351 (3.71); 0.1 *N* NaOH, 279 (4.56), 318 s (3.18), 360 s (3.69).

Anal. Calcd for $C_{10}H_{11}N_3O$: C, 63.48; H, 5.80; N, 22.19. Found: C, 63.49; H, 5.70; N, 22.12.

Preparation of Hydrazones.—Equimolar amounts of the hydrazine and aldehyde or ketone were refluxed in ethanol for 0.5–5 hr to precipitate the hydrazones, generally yellow solids. Aldehydes reacted more quickly than ketones. Filtration of the products and recrystallization, generally from benzene, gave 80–95% yields of the compounds listed in Table I. Absorption spectra of some of these hydrazones were determined as follows for the carbonyl compound; λ_{max}^{EtOH} [mμ (log ε)]: 7-formyl-8-quinolinol, 249 (4.33), 290 s (4.27), 306 (4.40), 381 (4.37), 436 (3.69); 5-acetyl-8-quinolinol, 243 (4.51), 289 (4.46), 359 (4.12); 2-formylpyridine, 238 (4.19), 264 (4.17), 274 s (4.12), 318 s (4.34), 352 (4.45), 439 s (3.30).

TABLE I

HYDRAZONES FROM 2-HYDRAZINO-8-QUINOLINOL AND CARBONYL COMPOUNDS

Carbonyl compd	Mp, °C[a]	Formula	% carbon Calcd	% carbon Found	% hydrogen Calcd	% hydrogen Found	% nitrogen Calcd	% nitrogen Found
5-Acetyl-8-quinolinol	218	$C_{20}H_{16}N_4O_2$	69.75	69.60	4.68	4.75	16.26	16.10
5-Acetyl-2-methyl-8-quinolinol	207	$C_{21}H_{18}N_4O_2$	70.38	70.45	5.06	5.20	15.63	15.83
4-Formyl-8-quinolinol	292	$C_{19}H_{14}N_4O_2$	69.93	69.24	4.32	4.40	15.94	16.15
5-Formyl-2-methyl-8-quinolinol	233	$C_{20}H_{16}N_4O_2$	69.75	69.57	4.68	4.84	16.26	16.11
7-Formyl-8-quinolinol	289	$C_{19}H_{14}N_4O_2$	69.93	70.08	4.32	4.52	15.94	16.08
7-Formyl-2-methyl-8-quinolinol	277	$C_{20}H_{16}N_4O_2$	69.75	69.53	4.68	4.83	16.26	16.14
7-Formyl-5-methyl-8-quinolinol	268	$C_{20}H_{16}N_4O_2$	69.75	69.92	4.68	4.91	16.26	16.09
Salicylaldehyde	239	$C_{16}H_{13}N_3O_2$	68.81	68.43	4.69	4.75	15.04	14.77
p-Dimethylaminobenzaldehyde	239	$C_{18}H_{18}N_4O$	70.58	70.30	5.92	6.14	18.28	17.98
Pentafluorobenzaldehyde	254	$C_{16}H_{18}F_5N_3O$	54.40	54.23	2.28	2.17	11.89	11.76
Phthalaldehydic acid	225	$C_{17}H_{13}N_3O_3$	66.45	66.64	4.26	4.46	13.67	13.47
2-Formylpyridine	214	$C_{15}H_{12}N_4O$	68.17	68.19	4.57	4.66	21.19	21.32
3-Formylpyridinium methiodide	231	$C_{16}H_{15}IN_4O$					13.79	14.60
4-Antipyrinecarboxaldehyde	248	$C_{21}H_{19}N_5O$	67.55	67.33	5.13	5.17	18.74	18.53
Salicylaldehyde[b]	206	$C_{17}H_{15}N_3O_2$	69.62	69.90	5.15	5.30	14.32	13.96

[a] Upper end of a 1–2° range. [b] Hydrazone of 2-(1-methylhydrazino)-8-quinolinol.

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[2] J. P. Phillips and J. T. Leach, *Anal. Chim. Acta*, **26**, 572 (1962).

[3] S. M. Atlas and H. F. Mark, *Angew. Chem.*, **72**, 249 (1960).

[4] Ultraviolet spectra were recorded on a Cary Model 14 spectrophotometer and infrared spectra on a Perkin-Elmer 337.

[5] J. P. Phillips, E. M. Barrall, and R. Breese, *Trans. Kentucky Acad. Sci.*, **17**, 138 (1956); *cf.* also K. Ramaiak and U. R. Srinvason, *Proc. Indian Acad. Sci.*, A**55**, 360 (1962).

[6] M. Hamana and K. Funakashi, *Yakagaku Zasshi*, **84**, 28 (1964); *Chem. Abstr.*, **61**, 3068 (1964).

3-Aminospirohydantoins

RICHARD A. WILDONGER[1] AND M. B. WINSTEAD

Department of Chemistry, Bucknell University, Lewisburg, Pennsylvania 17837

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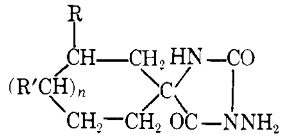
Some 3-amino-5,5-disubstituted hydantoins have a pronounced diuretic effect.[2] Such hydantoins have been prepared from the dihydrazide of α-substituted glycine-N-carboxylic acids,[2–5] and



I, $n = 0$; R = H
II, $n = 1$; R, R′ = H
III, $n = 2$; R, R′ = H
IV, $n = 3$; R, R′ = H
V, $n = 1$; R = CH_3; R′ = H
VI, $n = 1$; R = H; R′ = CH_3

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[1] National Science Foundation Undergraduate Research Participant, summer 1965.

[2] W. Taub, U. S. Patent 2,767,193 (1956); *Chem. Abstr.*, **51**, 5841 (1957).

[3] K. Schlögl, F. Wessely, O. Kraupp, and H. Storman, *J. Med. Pharm. Chem.*, **4**, 231 (1961).

[4] K. Schlögl, J. Derkosch, and E. Wawersich, *Monatsh.*, **85**, 607 (1954).