TABLE I
ARYLPHOSPHONIC AND DIARYLPHOSPHINIC ACIDS

Compd.	Yield, %	M.p., °C.[a]	Formula	Phosphorus, %[b] Calcd.	Found	Neut. equiv.[c] Calcd.	Found
p-Iodophenylphosphonic acid[d]	30	221–223	$C_6H_6IO_3P$	10.91	10.96	142.0	141.0
p-Acetylphenylphosphonic acid[e]	4,[f] 10[g]	163–167	$C_8H_9O_4P$	15.48	15.15	100.1	100.3
m-Phenoxyphenylphosphonic acid	45	92.5–93.5	$C_{12}H_{11}O_4P$	12.38	12.13	125.1	126.2
p-Phenoxyphenylphosphonic acid[h]	78	173.5–174.5	$C_{12}H_{11}O_4P$	12.38	12.34	125.1	124.9
2-Nitro-5-bromophenylphosphonic acid[i]	80	214–217 dec.[j]	$C_6H_5BrNO_5P$	10.98	10.99	141.0	140.2
Azoxydi-*p*-phenylenediphosphonic acid[k]	79	270–275 dec.	$C_{12}H_{12}N_2O_7P_2$	17.29	16.96	89.5	*l*
2-(*p*-Tolyloxy)phenylphosphonic acid	57	203–204	$C_{13}H_{13}O_4P$	11.72	11.55	132.1	133.6
2-(*p*-Tolyloxy)-*p*-tolylphosphonic acid	66	194–196	$C_{14}H_{15}O_4P$	11.13	11.03	139.1	141.4
Bis(*p*-iodophenyl)phosphinic acid	83	209–210	$C_{12}H_9I_2O_2P$	6.59	6.50	470.0	470.5
Bis(*p*-phenoxyphenyl)phosphinic acid	76	203–206	$C_{24}H_{19}O_4P$	7.70	7.53	402.4	398.5
4,4′-Phosphinicobis(3-bromobenzoic acid)[m]	46	278–282	$C_{14}H_9Br_2O_6P$	6.68	6.74	154.7	155.3

[a] Melting points were taken as previously described; *cf.* ref. 3. [b] Phosphorus was determined by the method of B. C. Stanley, S. H. Vannier, L. D. Freedman, and G. O. Doak, *Anal. Chem.*, **27,** 474 (1955). [c] The indicator used for the phosphonic acids was thymolphthalein; the indicator used for the phosphinic acids was phenolphthalein. [d] Previously prepared by G. M. Kosolapoff [*J. Am. Chem. Soc.*, **70,** 3465 (1948)] *via* the Sandmeyer reaction. [e] *Anal.* Calcd.: C, 48.01; H, 4.53. Found: C, 47.90; H, 4.34. [f] From *p*-acetylbenzenediazonium fluoroborate. [g] From *p*-aminophenylphosphonic acid. [h] Previously prepared as a monohydrate by W. C. Davies and C. J. O. R. Morris [*J. Chem. Soc.*, 2880 (1932)] *via* the Friedel–Crafts reaction. [i] *Anal.* Calcd.: Br, 28.34; N, 4.97. Found: Br, 28.38; N, 4.96. [j] This decomposition point was observed when a sample was placed on the melting point block preheated to 205° and the temperature of the block was slowly raised. [k] *Anal.* Calcd.: C, 40.24; H, 3.38; N, 7.82. Found: C, 39.94; H, 3.20; N, 7.60. [l] Determination of this neutral equivalent was not convenient because of the yellow color of dilute solutions of the compound. [m] *Anal.* Calcd.: Br, 34.44. Found: Br, 33.98.

TABLE II
ULTRAVIOLET ABSORPTION MAXIMA[a]

Compd.	λ_{max}, mμ	ϵ_{max}
p-Acetylphenylphosphonic acid	249	15,700
	284	1,600
m-Phenoxyphenylphosphonic acid	208	25,800
	272.5	1,960
	278.5	2,220
p-Phenoxyphenylphosphonic acid	236	15,700
	277.5	1,190
Bis(*p*-phenoxyphenyl)phosphinic acid	246.5	29,500
2-Nitro-5-bromophenylphosphonic acid	264.5	5,300
(Azoxydi-*p*-phenylene)diphosphonic acid	231.5	8,800
	268.5	9,880
	330	19,000

[a] All spectra were determined in 95% ethyl alcohol by the procedure previously described by H. H. Jaffé and L. D. Freedman, *J. Am. Chem. Soc.*, **74,** 1069 (1952).

phono group is very similar to that of the arsono group and also resembles that of the carboxy group, it seems reasonable to assume that the nitration of *m*-bromophenylphosphonic acid gives 2-nitro-5-bromophenylphosphonic acid.

Azoxydi-*p*-phenylenediphosphonic Acid.—A solution of *p*-nitrophenylphosphonic acid[3] (4.87 g.) in 25 ml. of water was added to a solution of 4.52 g. of arsenic oxide and 7.2 g. of NaOH in 25 ml. of water. The resulting mixture was refluxed for 8 hr. and then cooled. Acidification yielded a red precipitate which was recrystallized from a mixture of equal volumes of 95% ethanol and 6 *N* HCl. The ultraviolet absorption spectrum of this compound is similar to that of azoxybenzene,[13] which has maxima at 231 mμ (ε 8300), 260 (7000), and 323 (14,500).

Bis(*p*-iodophenyl)phosphinic Acid.—Bis(*p*-aminophenyl)phosphinic acid[5] (5.7 g.) in 25 ml. of water and 4.0 ml. of concentrated H_2SO_4 was diazotized at 0–5° with 3.5 g. of $NaNO_2$ in 6 ml. of water. The resulting solution was filtered from a trace of undissolved material and then added dropwise to a solution of 17.5 g. of KI and 17.5 g. of iodine in 25 ml. of water. The reaction mixture was stirred for 18 hr. at room temperature, and the precipitate of crude product was removed by filtration. It was purified by suspension in 100 ml. of 10% aqueous sodium bisulfite and subsequent recrystallization from 50% aqueous ethanol.

4,4′-Phosphinicobis(3-bromobenzoic Acid).—Bis(2-bromo-*p*-tolyl)phosphinic acid[9] (5.0 g.), dissolved in a mixture of 25 ml. of pyridine and 15 ml. of water, was oxidized with 25 g. of $KMnO_4$ by the method of Morgan and Herr.[14] After the excess pyridine was removed by steam distillation, the reaction mixture was filtered, decolorized with charcoal, and evaporated to 100 ml. on the steam bath. The resulting solution was added slowly with good stirring to 100 ml. of 10% HCl, whereupon the crude carboxy compound separated from solution. It was purified by recrystallization from aqueous acetone.

Acknowledgment.—The authors wish to acknowledge the technical assistance of Mrs. Joyce E. Carevic, Mr. Michael E. Beard, and Mr. Bobby R. Ezzell.

(13) P. H. Gore and O. H. Wheeler, *J. Am. Chem. Soc.*, **78,** 2160 (1956).
(14) P. W. Morgan and B. C. Herr, *ibid.*, **74,** 5264 (1952).

Substituted 1,4-Diazepin-2-ones

RUDDY LITTELL AND DUFF S. ALLEN, JR.

Organic Chemical Research Section,
Lederle Laboratories Division,
American Cyanamid Company, Pearl River, New York

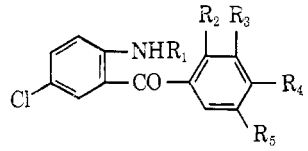
Received June 3, 1965

In view of current interest in 1,4-benzodiazepin-2-ones as psychotherapeutic agents,[1] a program to prepare novel analogs to be screened for pharmacological activity was initiated. Since the procedures used to prepare these analogs were essentially those described in the literature,[2] no experimental details are herein presented.

Compounds I and II (Table I) were prepared by Friedel–Crafts reactions.[2] Compounds III, IV, and V (Table I) were prepared from 6-chloro-2-methyl-4H-3,1-benzoxazin-4-one[3] by Grignard syntheses[2b,4] in yields of 20 (including hydrolysis), 38, and 39%, respectively. The preparation of the Grignard reagents from the appropriately substituted bromobenzenes failed in ethyl ether but proceeded satisfactorily in refluxing tetrahydrofuran.[5] The acetamides obtained as Grignard products

(1) S. J. Childress and M. I. Gluckman, *J. Pharm. Sci.*, **53,** 577 (1964), and references cited therein.
(2) (a) L. H. Sternbach, E. Reeder, O. Keller, and W. Metlesics, *J. Org. Chem.*, **26,** 4488 (1961); (b) L. H. Sternbach, R. I. Fryer, W. Metlesics, G. Sach, and A. Stempel, *ibid.*, **27,** 3781 (1962).
(3) A. J. Tomisek and B. E. Christensen, *J. Am. Chem. Soc.*, **70,** 2423 (1948).
(4) W. C. Lothrop and P. A. Goodwin, *ibid.*, **65,** 363 (1943).
(5) W. J. Gensler and J. E. Stauffer [*J. Org. Chem.*, **23,** 908 (1958)] reported their failure to prepare 3,4-methylenedioxyphenylmagnesium bromide and cited the difficulty of others in preparing organomagnesium compounds from the related 4-bromo- and 4-iodoveratroles.

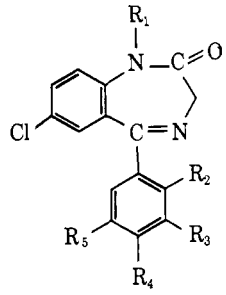
TABLE I
SUBSTITUTED *o*-AMINOBENZOPHENONES



Compd.	R_1	R_2	R_3	R_4	R_5	M.p., °C.[a]	Recrystn. solvent[b]	Formula	% calcd. C	H	Cl	N	% found C	H	Cl	N
I	H	H	Cl	Cl	H	103–105	E–H	$C_{13}H_8Cl_3NO$	52.04	2.68	35.45	4.67	51.4	2.80	35.4	4.91
II	H	H	CH_3	H	CH_3	102–105	E–H	$C_{15}H_{14}ClNO$	69.36	5.43	13.65	5.39	68.6	5.36	13.6	5.67
III	H	H	OCH_2O		H	70–74	M–W	$C_{14}H_{16}ClNO_3$	61.00	3.66	12.86	5.08	61.2	3.89	12.9	5.33
IV	Ac	CH_3	H	CH_3	H	104–105	E–M	$C_{17}H_{16}ClNO_2$	67.65	5.35	11.75	4.64	67.7	5.52	11.9	4.61
V	Ac	H	H	C_6H_5	H	163–165	D–M	$C_{21}H_{16}ClNO_2$	72.10	4.61	10.14	4.00	72.1	4.77	10.5	3.97
Va	H	H	H	C_6H_5	H	167–169	M	$C_{19}H_{14}ClNO$	74.14	4.59	11.52	4.55	73.9	4.74	11.0	4.53

[a] All melting points are uncorrected. [b] A = ethyl acetate, B = benzene, D = dichloromethane, E = ether, H = hexane, M = methanol, W = water.

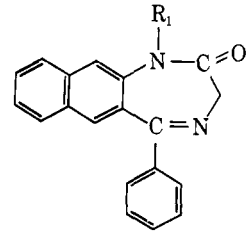
TABLE II
SUBSTITUTED 1,4-BENZODIAZEPIN-2-ONES



Compd.	R_1	R_2	R_3	R_4	R_5	M.p., °C.[a]	Recrystn. solvent[b]	Formula	% calcd. C	H	Cl	N	% found C	H	Cl	N
VI	H	H	Cl	Cl	H	245–247	D–M	$C_{15}H_9Cl_3N_2O$	53.07	2.68	31.32	8.25	52.7	2.67	31.3	8.49
VIa	CH_3	H	Cl	Cl	H	154–157	M	$C_{16}H_{11}Cl_3N_2O$	54.33	3.13	30.08	7.92	54.3	3.47	30.2	8.05
VII	H	H	CH_3	H	CH_3	240–242	D–H	$C_{17}H_{16}ClN_2O$	68.34	5.06	11.88	9.37	68.2	5.39	12.1	9.28
VIII	H	CH_3	H	CH_3	H	210–212	E–H	$C_{17}H_{15}ClN_2O$	68.34	5.06	11.88	9.37	68.3	5.35	12.2	9.69
VIIIa	CH_3	CH_3	H	CH_3	H	174–176	D–H	$C_{18}H_{17}ClN_2O$	69.83	5.47	11.33	8.96	69.1	5.77	11.8	9.07
IX	H	H	H	C_6H_5	H	272–275	A	$C_{21}H_{15}ClN_2O$	72.72	4.36	10.22	8.07	72.6	4.60	10.2	8.14
IXa	CH_3	H	H	C_6H_5	H	187–189	D–M	$C_{22}H_{17}ClN_2O$	73.22	4.75	9.83	7.76	72.8	4.81	9.83	7.51
X	H	H	OCH_2O		H	207–210	D–B	$C_{16}H_{11}ClN_2O_3$	61.06	3.52	11.27	8.90	61.4	3.83	11.7	9.05
Xa	CH_3	H	OCH_2O		H	145–147	D–H	$C_{17}H_{13}ClN_2O_3$	62.10	3.98	10.79	8.52	62.1	4.29	11.2	8.38

[a] All melting points are uncorrected. [b] A = ethyl acetate, B = benzene, D = dichloromethane, E = ether, H = hexane, M = methanol, W = water.

TABLE III
1,3-DIHYDRO-5-PHENYL-2H-NAPHTHO[2,3-*e*]-1,4-DIAZEPIN-2-ONES



Compd.	R_1	M.p., °C.[a]	Recrystn. solvent[b]	Formula	% calcd. C	H	N	% found C	H	N
XI	H	276–278	A	$C_{19}H_{14}N_2O$	79.70	4.93	9.78	79.5	4.96	9.68
XIa	CH_3	153–155	E–H	$C_{20}H_{16}N_2O$	79.98	5.37	9.33	79.5	5.49	9.28

[a] All melting points are uncorrected. [b] A = ethyl acetate, E = ether, H = hexane.

were hydrolyzed by heating in equal volumes of 6 *N* HCl and ethanol.[2b]

The substituted benzodiazepines VI–X (Table II) were prepared by condensation of the appropriate aminobenzophenones with ethyl glycinate hydrochloride in refluxing pyridine.[6] The naphthodiazepin-2-one (XI) (Table III) was prepared in the same manner from 3-(2-amino)naphthyl phenyl ketone.[4] Methylations of the 1,4-aryldiazepin-2-ones were effected by treatment with methyl iodide or dimethyl sulfate and base.[7]

The compounds herein described showed no interesting pharmacological activities.[8]

Acknowledgment.—We wish to thank Mr. L. Brancone and associates for the microanalyses and Messrs. W. Fulmor and G. Morton for their generous assistance with the interpretation of the spectral data.

(6) L. H. Sternbach, R. I. Fryer, W. Metlesics, E. Reeder, G. Sach, G. Saucy, and A. Stempel, *J. Org. Chem.*, **27**, 3788 (1962).

(7) L. H. Sternbach and E. Reeder, *ibid.*, **26**, 4936 (1961).

(8) Private communication from Dr. A. C. Osterberg of the Experimental Therapeutics Research Section of these laboratories.