TABLE I[a]

No.	b	c	R	Y	Mp, °C[d]	Solvent of recrystn	Formula	Calcd, % C	H	N	P	S	Found, % C	H	N	P	S
Diethyl Phosphoryl Esters of Quinolinols, Hydroxystilbazoles, 4,4′-Hydroxydihydrostilbazole, and 4-(3-Pyridylazo)phenol																	
1	3	...	H	...	159	EtOH											
2	3	...	CH_3	...	111[e]	H_2O											
3	5	...	H	...	157	MeOH											
4	5	...	CH_3	...	117	MeOH–Et_2O	$C_{20}H_{21}N_4O_{11}P$	45.81	4.04	10.69	5.91		46.23	3.96	10.56	5.72	
5	6	...	H	...	178	MeOH											
6	6	...	CH_3	...	137	MeOH	$C_{20}H_{21}N_4O_{11}P$	45.81	4.04	10.69	5.91		46.00	3.83	10.54	5.87	
7	7	...	H	...	168	MeOH											
8	7	...	CH_3	...	92	MeOH	$C_{20}H_{21}N_4O_{11}P$	45.81	4.04	10.69	5.91		46.27	3.95	10.70	6.01	
9	8	...	H	...	123	H_2O											
10	8	...	CH_3	...	107	H_2O	$C_{20}H_{21}N_4O_{11}P$	45.81	4.04	10.69	5.91		45.86	4.43	10.68	5.96	
11	5[f]	...	H	...	141	MeOH											
12	5[f]	...	CH_3	...	133	MeOH											
13	5[f]	...	CH_3	...	129[g]	Me_2CO	$C_{21}H_{26}NO_7PS$	53.95	5.61	3.00	6.63	6.86	53.79	5.37	2.97	6.34	6.47
14	4	2	H	CH=CH	154	MeOH											
15	4	2	CH_3	CH=CH	157	MeOH	$C_{24}H_{25}N_4O_{11}P$	50.01	4.37	9.72	5.37		49.95	4.04	9.88	5.38	
16	4	3	H	CH=CH	163	MeOH											
17	4	3	CH_3	CH=CH	127	MeOH	$C_{24}H_{25}N_4O_{11}P$	50.01	4.37	9.72	5.37		50.05	3.86	9.66	5.44	
18	4	4	H	CH=CH	141	MeOH											
19	4	4	H	CH=CH	121[g]	Me_2CO–Et_2O											
20	4	4	CH_3	CH=CH	152	MeOH											
21	4	4	CH_3	CH=CH	168	Me_2CO	$C_{28}H_{30}NO_7PS$	57.79	5.82	2.70	5.96	6.17	57.75	5.76	2.90	5.80	6.06
22	4	4	H	CH_2CH_2	103	MeOH–H_2O											
23	4	4	CH_3	CH_2CH_2	77	MeOH–H_2O	$C_{24}H_{27}N_4O_{11}P$	49.83	4.71	9.69	5.36		49.68	4.81	9.67	5.25	
24	3	4	H	N=N	133	MeOH											
25	3	4	H	N=N	115[g]	MeOH–Et_2O											
26	3	4	CH_3	N=N	104	EtOH	$C_{22}H_{23}N_6O_{11}P$	45.68	4.01	14.53	5.36		45.85	4.40	14.35	5.31	
Bisquaternary Compounds Containing the Bridge CH_2OCH_2 between the Two Ring Nitrogen Atoms																	
27	6	...	...	...	193	Me_2CO											
28	5[f]	...	...	...	134	EtOH–Me_2CO	$C_{46}H_{46}N_8O_{23}P_2$	45.20	3.79	10.55	5.83		44.95	3.67	10.70	5.88	
29	4	2	...	CH=CH	197	MeOH	$C_{48}H_{48}N_8O_{23}P_2$	49.41	4.15	9.60	5.31		50.20	4.68	9.78	4.57	
30	4	3	...	CH=CH	129	MeOH	$C_{48}H_{48}N_8O_{23}P_2$	49.41	4.15	9.60	5.31		49.26	4.21	9.63	4.92	
31	4	4	...	CH=CH	192	MeOH	$C_{48}H_{48}N_8O_{23}P_2$	49.41	4.15	9.60	5.31		49.64	4.48	9.39	5.29	
32	4	4	...	CH_2CH_2	87	MeOH											

[a] The formula weight of all compounds except those containing CH=CH and N=N, which were not tested, was correct to 1.5% by the picrate method. [b] This number refers to the quinoline or pyridine rings. [c] This number refers to the benzene ring. [d] Melting points were taken on a Uni-Melt apparatus. [e] Previously reported;[2] softens at 108–110°, melts at 135–137°. [f] Isoquinolinol. [g] *p*-Toluenesulfonate.

added a few minutes later, and much of the solvent was evaporated at room temperature. The crude picrate was obtained by cooling and was recrystallized from methanol.

Analysis for Picrate.—All the picrates except those containing the chromophores CH=CH and N=N were analyzed by measuring the optical density at 415 mμ of a solution at about 2×10^{-5} *M* in 10% ethanol. The method was standardized with picric acid and a few drops of dilute alkali. All compounds were correct with ±1.5% which is about the accuracy of the method. The identity of the unquaternized esters in those compounds containing a chromophore rests upon the correct analyses of the quaternized derivatives.

6,12-Diphenyldibenzo[*b*,*f*][1,5]diazocines

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Since 2,8-dichloro-6,12-diphenyldibenzo[*b*,*f*][1,5]diazocine was shown to have hormonelike activity,[1] a number of analogs were prepared. In two cases[2,3] 6,12-diphenyldibenzodiazocines were formed by heating the corresponding 2-aminobenzophenone hydrochlorides. We have found that dibenzodiazocines can be prepared conveniently and in good yields from 2-aminobenzophenones when Lewis acids are used as condensing agents.

Experimental Section

All melting points are corrected. Ultraviolet spectra were determined in isopropyl alcohol using a Cary 14 spectrophotometer.

General Procedure.[4]—The corresponding 2-aminobenzophenone was dissolved in an inert solvent, the catalyst was added, and the solution was heated under reflux for the time indicated. After cooling, the solution was washed with aqueous sodium hydroxide, and the solvent was removed *in vacuo*. In each case the crystalline reaction product was recrystallized from a mixture of methylene chloride and alcohol to give pale yellow prisms.

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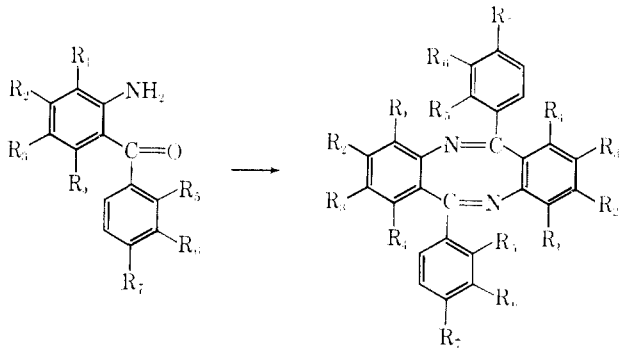
(1) Pharmacological data on some of the compounds described will be published at a later date; see also G. W. Duncan, S. C. Lyster, and J. B. Wright, *Proc. Soc. Exptl. Biol. Med.*, **120**, 725 (1965).

(2) A. Sondheimer, *Chem. Ber.*, **29**, 1272 (1896).

(3) A. Giacalone, *Gazz. Chim. Ital.*, **65**, 120 (1935); *Chem. Abstr.*, **29**, 5450[9] (1935).

(4) Variations of the condensing agents and solvents gave different yields of the respective product. One representative example for the preparation of each compound is shown in Table I on the following page.

TABLE I



Starting material[a] Structure	g	Solvent (ml)	Catalyst (ml)	Reaction time, hr	Yield %	Mp, °C	Formula	Product Calcd, % C	Calcd, % H	Found, % C	Found, % H	λ_{max}, mμ[b]	ε × 10^{-3}
R_1–R_7 = H	19.7	C_6H_5Cl (250)	$AlCl_3$ (7.5 g)	8	71	191–193	$C_{26}H_{18}N_2$[c]					256	35
R_3 = Cl[d]	20	Xylene (86)	BF_3–Et_2O (1.3)	6	88	217–219	$C_{26}H_{16}Cl_2N_2$[e]	73.08	3.77	73.37	3.86	260	38
R_3 = F[f]	0.5	C_6H_5Cl (15)	BF_3–Et_2O (0.05)	17	65	189–191	$C_{26}H_{16}F_2N_2$	79.17	4.09	79.17	3.69	258	34
R_3 = Br[h]	6.9	C_6H_5Cl (25)	BF_3–Et_2O (0.4)	16	23	231–234	$C_{26}H_{16}Br_2N_2$	60.48	3.12	60.48	2.98	260	43
R_3 = CF_3[i]	13.3	C_6H_6 (150)	$TiCl_4$ (2.2)	2	23	204–207	$C_{28}H_{16}F_6N_2$	67.96	3.26	68.07	3.23	260	39
R_3 = OCH_3[j]	3.9	C_6H_5Cl (80)	BF_3–Et_2O (0.2)	6	65	204–206	$C_{28}H_{22}N_2O_2$	80.36	5.30	80.56	5.72	255	38
R_3 = R_5 = Cl[k]	13.3	C_6H_5Cl (50)	$TiCl_4$ (2.7)	16	30	213–215	$C_{26}H_{14}Cl_4N_2$	62.93	2.84	63.21	2.85	*l*	
R_3 = Br, R_5 = F[f]	5.9	C_6H_5Cl (20)	BF_3–Et_2O (0.5)	16	63	232–234	$C_{26}H_{14}Br_2F_2N_2$	56.55	2.56	56.42	2.74	250	40
R_3 = Cl, R_5 = CH_3[j]	2.4	C_6H_5Cl (10)	$TiCl_4$ (0.4)	16	60	187–189	$C_{28}H_{20}Cl_2N_2$	73.85	4.43	73.94	4.72	259	29
R_3 = Cl, R_5 = OCH_3[j]	1.0	C_6H_5Cl (15)	BF_3–Et_2O (0.1)	16	13	258–260	$C_{28}H_{20}Cl_2N_2O_2$	69.00	4.14	68.85	4.19	*m*	
R_3 = R_6 = Cl[a]	13.3	C_6H_5Cl (50)	BF_3–Et_2O (0.7)	16	64	191–194	$C_{26}H_{14}Cl_4N_2$	62.93	2.84	62.97	3.02	255	40
R_3 = Cl, R_7 = F[f]	2.7	C_6H_5Cl (15)	BF_3–Et_2O (0.25)	16	76	252–254	$C_{26}H_{14}Cl_2F_2N_2$	67.40	3.05	67.19	2.82	261	37
R_3 = NO_2[a]	24.2	C_6H_5Cl (100)	$TiCl_4$ (5.8)	16	87	293–296	$C_{26}H_{16}N_4O_4$	69.64	3.60	69.93	3.82	291[n]	28
R_6 = Cl[a]	5.8	C_6H_5Cl (25)	BF_3–Et_2O[o] (1.5), $TiCl_4$ (1.3)	16	52	184–185	$C_{26}H_{16}Cl_2N_2$	73.08	3.77	73.25	4.00	255	37
R_2 = Cl[j]	46.4	C_6H_5Cl (200)	BF_3–Et_2O (2.6)	16	84	255–256	$C_{26}H_{16}Cl_2N_2$	73.08	3.77	73.40	3.53	255	39
R_4 = Cl[j]	11.6	C_6H_5Cl (50)	BF_3–Et_2O (0.65)	16	52	244–245	$C_{26}H_{16}Cl_2N_2$	73.08	3.77	73.38	3.99	259	38
R_1 = R_3 = Br[a]	18.0	C_6H_5Cl (50)	BF_3–Et_2O[o] (3.2), $TiCl_4$ (2.6)	16	63	273–274	$C_{26}H_{14}Br_2N_2$	46.33	2.09	46.39	2.17	262	43
R_2 = R_3 = Cl[k]	8.0	C_6H_5Cl (30)	BF_3–Et_2O (0.4)	16	64	350–352	$C_{26}H_{14}Cl_4N_2$	62.93	2.84	63.05	3.09	260	40

[a] R = H unless indicated otherwise. [b] All compounds with the exceptions indicated showed a shoulder or maximum at *ca.* 320 mμ (ε 5000–7000). [c] Known compound (see ref 2). [d] F. D. Chattaway, *J. Chem. Soc.*, **85**, 344 (1904). [e] Water was removed during the reaction with a Dean–Stark receiver. [f] Calcd: mol wt, 427. Found: mol wt, 445 (thermoosmosis). [g] J. F. J. Dippy and V. Moss, *J. Chem. Soc.*, 2205 (1952). [h] A. Angel, *ibid.*, **101**, 515 (1912). [i] G. Sadey and L. H. Sternbach, *Helv. Chim. Acta*, **45**, 2226 (1962). [j] L. H. Sternbach, R. I. Fryer, W. Metlesics, G. Sach, and A. Stempel, *J. Org. Chem.*, **27**, 3781 (1962). [k] L. H. Sternbach, E. Reeder, O. Keller, and W. Metlesics, *ibid.*, **26**, 4488 (1961). [l] λ 250 mμ (infl) (ε 27,000) and *ca.* 310 mμ (sh) (ε 5500). [m] λ 260 mμ (infl) (ε 21,000) and λ_{max} 307 mμ (ε 14,000). [n] This aminobenzophenone was prepared by Mr. L. A. Dolan according to method A; lit.[j] mp 107–109°. *Anal.* Calcd for $C_{13}H_9Cl_2NO$: C, 58.67; H, 3.41. Found: C, 58.97; H, 3.88. [o] K. Schofield and R. S. Theobald, *J. Chem. Soc.*, 1505 (1950). [p] Also 335 mμ (infl) (ε 19,000). [q] M. W. G. Coldham, J. W. Lewis, and S. G. P. Plant, *J. Chem. Soc.*, 4530 (1954). [r] Use of either of the two catalysts separately did not give satisfactory yields. [s] P. Ruggli and B. Hegedüs, *Helv. Chim. Acta*, **24**, 703 (1941).

The Preparation of 5-Substituted 5-(2-Naphthyl)hydantoins as Potential Anticonvulsants

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Previous research by Henze and Nunn,[2] on the synthesis of selected 5-substituted 5-(1-naphthyl)hydantoins as potentially efficacious anticonvulsant compounds[3] has suggested the preparation of a series of 5-substituted 5-(2-naphthyl)hydantoin analogs.

Experimental Section

2-Naphthyl Ketone Precursors.—Each ketone was prepared by the interaction of 2-naphthoyl chloride with the appropriate organocadmium reagent. Table I lists previously unreported 2-naphthyl ketones.

5-Substituted 5-(2-Naphthyl)hydantoin Synthesis.—A modified Bücherer–Bergs reaction was utilized for the preparation of each hydantoin. In a 300-ml glass liner of a screw-top Monel metal bomb 0.01 mole of a 2-naphthyl ketone was dissolved in 100 ml of dimethylformamide. Following the addition of a solution of 1.5 g formula weights of KCN in the least amount of water, 4.0 equiv of $(NH_4)_2CO_3$ was introduced and the bomb was rapidly closed. The resulting reaction mixture was placed in an oven (115°) for 24 hr, then made alkaline by the addition of 10% aqueous NaOH. Any unreacted ketone was subsequently removed by ether extraction. Acidification of the aqueous layer with concentrated HCl precipitated the desired hydantoin, which was recrystallized to white needles from EtOH–H_2O. Results are indicated in Table II.

TABLE I

SUBSTITUTED 2-NAPHTHYL KETONES

R	Bp (mm) or mp,[a] °C	Yield, %	Calcd, % C	Calcd, % H	Found,[b] % C	Found,[b] % H
sec-C_4H_9	168–170 (7)	62	84.86	7.60	85.05	7.71
t-C_4H_9	189–191 (15)	39	84.86	7.60	84.57	7.68
i-C_5H_{11}	45–45.4	61	84.91	8.02	84.63	8.16
n-$C_{12}H_{25}$	51–52	73	85.10	9.98	85.18	9.88

[a] All melting points were determined by the capillary method and are corrected. [b] Carbon and hydrogen microanalyses were performed by the Huffman Laboratories, Inc., Wheatridge, Colo.

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(2) H. R. Henze and L. Nunn, *J. Org. Chem.*, **12**, 540 (1947).
(3) H. H. Merritt and T. J. Putnam, *Epilepsia*, 51 (1945).