TABLE I
9-ALKYLAMINO AND SUBSTITUTED-ALKYLAMINO 1,2,3,4-TETRAHYDROACRIDINE HYDROCHLORIDES

Substituent	% yield	M.p., °C.[a]	Formula	C, % Calcd.	C, % Found	H, % Calcd.	H, % Found	Cl, % Calcd.	Cl, % Found	N, % Calcd.	N, % Found
9-Methylamino	47.5	297–300	$C_{14}H_{17}ClN_2$	67.6	67.7	6.9	6.8	14.3	14.6	11.3	11.6
9-Butylamino	57.5	200–203	$C_{17}H_{23}ClN_2$	70.2	70.4	7.9	8.2	12.2	12.2	9.6	9.6
9-Allylamino	53.3	228–231	$C_{16}H_{19}ClN_2$	69.9	69.7	7.0	7.6	12.9	12.7	10.2	10.5
9-Benzylamino[b]	47.5	252–254	$C_{20}H_{21}ClN_2$	73.9	73.7	6.5	6.7	10.9	10.8	8.6	8.6
9-(2-Phenethyl)amino	52.2	216–218	$C_{21}H_{23}ClN_2$	74.4	74.2	6.8	6.8	10.5	10.4	8.3	8.3

[a] Considerable product precipitated out with the benzylamine hydrochloride in the original reaction. [b] All melting points are uncorrected and determined in a Fisher-Johns melting point apparatus.

tinued for 3 hr. The reaction mixture was cooled, and 700 ml. of ether was added. The butylamine hydrochloride which precipitated was filtered and the filtrate was extracted with three 100-ml. portions of 20% NaOH solution. The ether solution, which contained the product, was dried ($MgSO_4$) and filtered. The ether was then distilled, and the residue was washed with hexane to give 14.0 g. of crude 9-butylamino-1,2,3,4-tetrahydroacridine which melted at 60–62°. Recrystallization of a small portion of the crude product from hexane gave crystals, m.p. 63–65°. The 9-butylamino-1,2,3,4-tetrahydroacridine was dissolved in dilute aqueous HCl. The resulting clear solution was evaporated to dryness at 50° under reduced pressure and the residue was recrystallized from isopropyl alcohol to give 11.5 g. of hydrochloride, m.p. 200–203°.

The other compounds were made with appropriate modifications of the general method described above and recrystallized from isopropyl or absolute ethyl alcohol.

7- and 12-(*o*-Halophenyl)benz[*a*]anthracenes[1a]

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The title compounds were prepared as part of a program to make substituted benz[*a*]anthracenes available for antitumor screening. The synthetic routes to these compounds involve extensions to useful reactions previously recorded.

Experimental[3-5]

Two typical experiments are described.

2-(1-Naphthylmethyl)-2′-chlorobenzophenone.—The Grignard reagent prepared from 11.8 g. (0.04 mole) of 2-(1-naphthylmethyl)bromobenzene and 1.22 g. (0.05 g.-atom) of magnesium in dry ether was added slowly to a boiling solution of 6.61 g. (0.04 mole) of 2-chlorobenzoyl chloride in toluene. Ether was allowed to distil until the boiling point of the solution reached 105°, and the solution was heated an additional 3 hr. The solution was cooled, decomposed with cold 25% sulfuric acid, and worked up in the usual way. The low-boiling fractions were removed under reduced pressure and the residue[6] was triturated with ethyl ether giving 0.3 g. of 7-(2-chlorophenyl)benz[*a*]anthracene which was removed. The dark oil was chromatographed on a 30.5-cm. column of Florisil, then on a column of basic alumina, and again on Florisil yielding 3.55 g. (25%) of light, yellow oil which crystallized[7] on standing 3 days (see Table I).

7-(2-Chlorophenyl)benz[*a*]anthracene (I).—A mixture of 1 g. (0.003 mole) of 2-(1-naphthylmethyl)-2′-chlorobenzophenone, 60 ml. of glacial acetic acid, and 15 ml. of 48% HBr was sealed in a Carius tube and heated for 7 hr. at 180°.[8] The usual work-up plus elution chromatography on basic alumina using 30–60° petroleum ether as the eluent finally gave a crystalline material which on recrystallization from 95% ethanol had a constant m.p. of 165–166°[9] (see Table II).

TABLE I
NEW KETONES

Compd.	% yield	M.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Halogen, % Calcd.	Halogen, % Found
2-(1-Naphthylmethyl)-2′-chlorobenzophenone*	25	90–91	80.78	80.53	4.80	4.77	9.94	9.50
2-(1-Naphthylmethyl)-2′-fluorobenzophenone*	20	54–55	84.69	84.46	5.03	4.96	5.58	5.47
2-(2-Naphthylmethyl)-2′-chlorobenzophenone	38	104–107	80.78	80.41	4.80	4.91	9.94	10.16
2-(2-Naphthylmethyl)-2′-fluorobenzophenone	37	73–74	84.69	84.54	5.03	5.18	5.58	5.72

TABLE II
NEW BENZ[*a*]ANTHRACENES

Compd.	% yield	M.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Halogen, % Calcd.	Halogen, % Found
7-(2-Chlorophenyl)benz[*a*]anthracene (I)*	42	165–166	85.07	85.16	4.47	4.47	10.46	10.42
7-(2-Fluorophenyl)benz[*a*]anthracene (II)*	87	154–155	89.42	89.43	4.69	4.67	5.89	5.80
12-(2-Chlorophenyl)benz[*a*]anthracene (III)	91	144–145	85.07	84.74	4.47	4.29	10.46	10.62
12-(2-Fluorophenyl)benz[*a*]anthracene (IV)	79	127–128	89.42	88.93	4.69	4.75	5.89	5.90

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(2) F. A. Vingiello, M. O. L. Spangler, and J. Bandurant, *J. Org. Chem.*, **25**, 2091 (1960).

(3) Analyses were performed by Geller Laboratories, Bardonia, N. Y., except those marked with an asterisk which were performed by Galbraith Laboratories, Knoxville, Tenn.

(4) Melting points are corrected, boiling points are not.

(5) All g.p.c. analyses were performed on a Micro-Tek Model 1400 gas chromatograph equipped with a 152.4 × 3.02 cm. (5 ft. × 1/8 in.) column packed with 5% SE-30 on Chromosorb W (60–80 mesh) operated at a column temperature of 280°, inlet temperature of 330°, and using a hydrogen flame detector.

(6) The product decomposed when an attempt was made to distil it under reduced pressure. The experiment had to be repeated.

(7) This material showed only one peak on g.p.c. analysis, whereas the crude material showed three peaks.

(8) Attempted cyclization employing the usual reflux procedure resulted in recovery of starting material.

(9) The ultraviolet and visible spectra of I and II were taken on a Model 3000 Spectracord and the spectra of III and IV were taken with a Beckman DK-2A ratio recording spectrophotometer at 10 mg./l. in 95% ethanol. The wave-length maxima in mμ are for I: 221, 230, 254, 258, 270, 280, 292, 300, 329, 335, and 345; for II: 221, 230, 254, 258, 270, 280, 292, 300, 320, 334, 345; for III: 226, 291, 269, 277, 289, 320, 335, 345; for IV: 225, 258, 268, 278, 289, 320, 335, and 345.