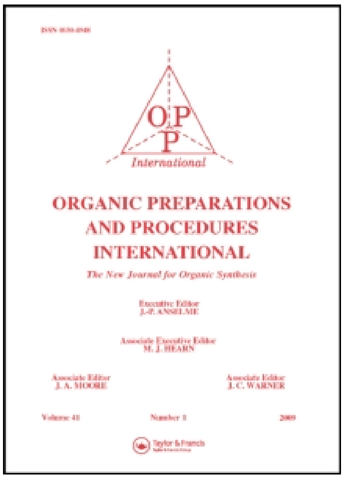

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4-(7-BENZ[a]ANTHRACENYL)-N-(2-SUBSTITUTED ETHYL)BENZAMIDES

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4-(7-BENZ[a]ANTHRACENYL)-N-(2-SUBSTITUTED ETHYL)BENZAMIDES

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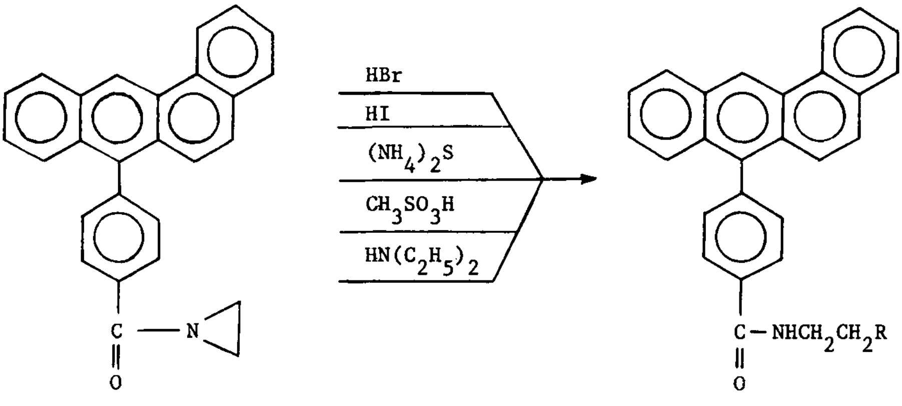
We have recently reported[2] the preparation of four new polycyclic 1-aroylaziridines, 3- and 4-(7-benz[a]anthracenyl)- and 3- and 4-(9-anthracenyl)-N-benzoylaziridines, and their conversion to the corresponding 2-oxazolines[3] and 2-thiazolines.[4] The characteristic chemical reactivity of these new polycyclic 1-aroylaziridines is further demonstrated by the conversion of 4-(7-benz[a]anthracenyl)-N-benzoylaziridine (I) into several 4-(7-benz[a]anthracenyl)-N-(2-substituted ethyl)benzamide compounds by cleavage of the aziridine ring with various acids.[5]



I

#	II	III	IV	V	VI
-R	Br	I	SH	$N(C_2H_5)_2$	OSO_2CH_3

EXPERIMENTAL

The melting points of all compounds melting below 300° were taken on a Fisher-Johns melting point block; those melting above 300° were taken on a Mel-Temp capillary melting point apparatus. Analyses were performed by Galbraith Labs., Knoxville, Tennessee; M-H-W Labs., Garden City, Michigan; and on a F and M Scientific Corp., Model 185, C, H and N analyzer. The ir spectra were recorded on a Beckman IR-5 infrared spectrophotometer or a Perkin-Elmer Model 621 spectrophotometer using potassium bromide disks. The nmr spectra were recorded on a Varian A-60 spectrophotometer, using 10% deuterated chloroform or DMSO solutions with tetramethylsilane (TMS) as an internal standard.

4-(7-Benz[a]anthracenyl)-N-(2-bromoethyl)benzamide (II).

Anhydrous hydrogen bromide was bubbled vigorously through a solution of 3.0 g (0.008 mole) of I in 50 ml of chloroform at room temperature for 15 min. The solution was then transferred to a separatory funnel, washed successively with 50 ml of water, 50 ml of 10% sodium bicarbonate solution, twice with 50 ml portions of water, and the chloroform layer was separated and dried over sodium sulfate. The dried solution was filtered, concentrated, and the resultant white solid was recrystallized five times from benzene, affording 3.2 g (0.007 mole, 87%) of a white powder, mp 203-208°; ir (KBr) 3050, 2950, 1634 (C=O), multiplet 900-700 cm^{-1}; nmr (DMSO) δ 5.1-4.1 (m, 15, ArH), 1.99 (s, 4, CH_2-CH_2).

Anal. Calcd for $C_{27}H_{20}BrNO$: C, 71.36; H, 4.45; N, 3.08; Br, 17.59.
Found: C, 71.50; H, 4.38; N, 3.27; Br, 17.88.

4-(7-Benz[a]anthracenyl)-N-(2-iodoethyl)benzamide (III).

A mixture of 3.0 g (0.008 mole) of I in 50 ml of benzene and 10 ml of 45% aqueous hydriodic acid was magnetically stirred at 0° for 15 min. The benzene layer was separated and diluted with benzene to a volume of 100 ml, then washed successively with 50 ml of water, 50 ml of 10% sodium bicarbonate solution, twice with 50 ml portions of water, separated and dried over sodium sulfate. After 15 min the dried solution was filtered, concentrated, and the resultant viscous semi-solid was recrystallized five times from ethyl acetate. This afforded 3.0 g (0.0058 mole, 73%) of a light yellow powder, mp 196-198°; ir (KBr) 3050, 2950, 1634 (C=O), multiplet 900-700 cm^{-1}; nmr (DMSO) δ 5.1-4.1 (m, 15, ArH), 2.0 (s, 4, CH_2-CH_2).

Anal. Calcd for $C_{27}H_{20}NIO$: C, 64.69; H, 4.03; N, 2.79; I, 25.31.

Found: C, 64.45; H, 3.80; N, 2.51; I, 25.04.

4-(7-Benz[a]anthracenyl)-N-(2-thiolethyl)benzamide (IV).

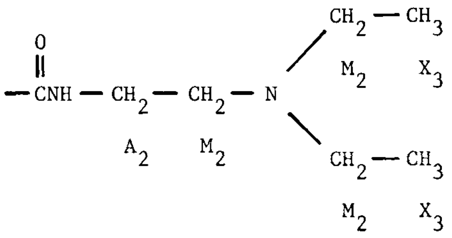
This is essentially the procedure of Goldberg and Kelly.[6] A mixture of 3.0 g (0.008 mole) of I in 100 ml of tetrahydrofuran (THF) and 50 ml of 45% aqueous ammonium sulfide was stirred at room temperature for 12 hrs. The mixture was then transferred to a separatory funnel, the aqueous layer saturated with sodium chloride, and the THF layer separated, washed successively with 50 ml of water, 50 ml of 10% sodium bicarbonate solution and twice with 50 ml portions of water (each water washing was saturated with sodium chloride). The THF layer was separated, dried over sodium sulfate for 15 min, filtered and concentrated to give a viscous pale reddish-brown oil which was dissolved in 50 ml of ethyl acetate, cooled overnight and the precipitated product filtered. The product which was now insoluble in benzene, ethyl acetate, chloroform and THF, was recrystallized five times from DMSO-absolute ethanol (6:4). This afforded 1.2 g (0.0035 mole, 43%) of a light yellow powder, mp 304-306°; ir (KBr) 3050, 2920, 1645 (C=O), multiplet 900-700 cm^{-1}, (the sulfur-hydrogen stretching frequency which is characteristically weak and in the region 2600-2500 cm^{-1},[7] was not detected); nmr (DMSO) δ 5.2-4.1 (m, 15, ArH), 2.09 (m, 2, CH_2), 1.75 (m, 2, CH_2), 1.37 (s, 1, SH).

Anal. Calcd for $C_{27}H_{21}NOS$: C, 79.53; H, 5.24; N, 3.44; S, 7.86.

Found: C, 79.33; H, 5.15; N, 3.53; S, 8.37.

4-(7-Benz[a]anthracenyl)-N-(2-diethylaminoethyl)benzamide (V).

Using the procedure of Thyrum and Day,[8] a mixture of 3.0 g (0.008 mole) of I and 1.2 g (0.016 mole) of diethylamine in 50 ml of benzene was refluxed for 12 hrs, the solution concentrated, and the resultant viscous oil was crystallized from ethyl acetate. Four recrystallizations of the product from ethyl acetate afforded 2.7 g (0.0061 mole, 76%) of white feathery needles, mp 164-166°; ir (KBr) 3050, 2960, 1625 (C=O), multiplet 900-700 cm^{-1}; nmr ($CDCl_3$) δ 5.0-4.0 (m, 15, ArH), 1.96 (q, 2, A_2), 1.44 (q, 6, M_6), 0.59 (t, 6, X_6).



Anal. Calcd for $C_{31}H_{30}N_2O$: C, 83.36; H, 6.78; N, 6.27.

Found: C, 83.52; H, 6.85; N, 6.00.

4-(7-Benz[a]anthracenyl)-N-(2-methylsulfonylethyl)benzamide (VI).

A mixture of 3.0 g (0.008 mole) of I and 1.5 g (0.016 mole) of methanesulfonic acid in 75 ml of benzene was stirred at room temperature for 3 hrs, the solution was then concentrated and the resulting yellow solid was taken-up in 25 ml of ethyl acetate and filtered. The solid was washed with 100 ml of ether in 10 ml portions on the filter paper, and was then recrystallized five times from toluene-95% ethanol (7:3). This afforded 2.8 g (0.0059 mole, 74%) of a white powder, mp 236-238°; ir (KBr) 3050, 2950, 1720 (c=O), 1260, 1190, 1100, multiplet 900-700 cm^{-1}; nmr (DMSO) δ 5.2-4.1 (m, 15, ArH), 2.56 (m, 2, CH_2), 1.90 (m, 2, CH_2), 1.40 (s, 3, CH_3).

Anal. Calcd for $C_{28}H_{23}NO_4S$: C, 71.61; H, 4.95; N, 2.98; S, 6.83.

Found: C, 71.68; H, 5.07; N, 2.94; S, 6.54.

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