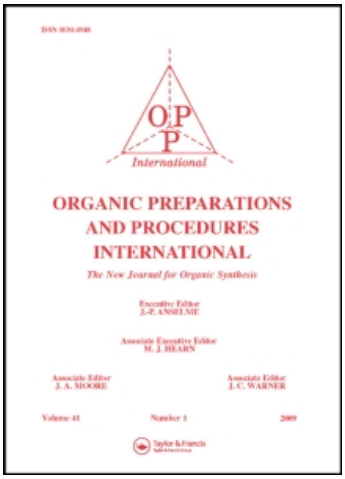

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3- AND 4-(7-BENZ[a]ANTHRACENYL)PHENYL-2-OXAZOLINES AND 3- AND 4-(9-ANTHRACENYL)PHENYL-2-OXAZOLINES AND THEIR HYDROCHLORIDE SALTS

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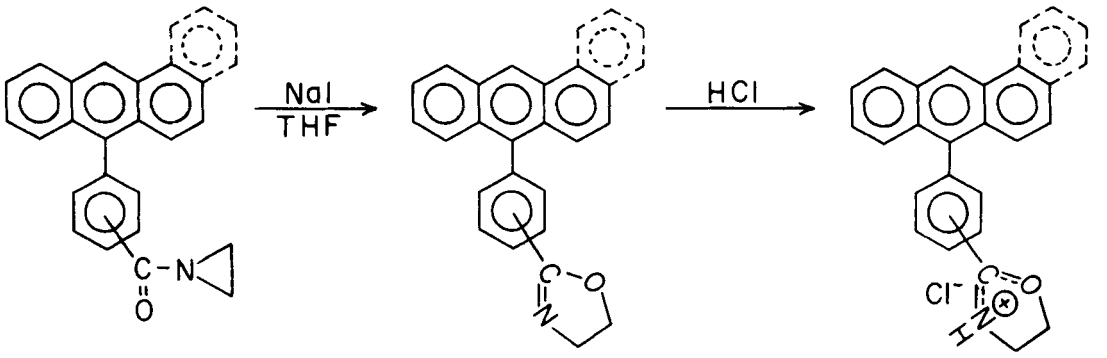
We have previously reported[2] the preparation of four polycyclic 1-aroylaziridines, 3- and 4-(7-benz[a]anthracenyl)-N-benzoylaziridines (1 and 2) and 3- and 4-(9-anthracenyl)-N-benzoylaziridines (3 and 4). We now report on the conversion of these benzoylaziridines to their respective 2-oxazolines[3,4,5] and 2-oxazoline hydrochloride salts.[4]

The four 2-oxazolines, 3- and 4-(7-benz[a]anthracenyl)phenyl-2-oxazolines (5 and 6) and 3- and 4-(9-anthracenyl)phenyl-2-oxazolines (7 and 8) were prepared in high yields from the corresponding benzoylaziridines by isomerization reactions catalyzed by sodium iodide (Chart I and Table I). Refluxing the benzoylaziridines in the absence of sodium iodide resulted in essentially no isomerization products being formed.

Under anhydrous conditions high molecular weight 2-oxazolines have been reported to form hydrochloride salts.[4] The four hydrochloride salts, 3- and 4-(7-benz[a]anthracenyl)phenyl-2-oxazoline hydrochlorides (9 and 10) and 3- and 4-(9-anthracenyl)phenyl-2-oxazoline hydrochlorides (11 and 12) were prepared by the addition of ethyl ether solutions saturated with anhydrous hydrogen chloride to anhydrous tetrahydrofuran solutions containing the four 2-oxazolines (Chart I and Table I).

CHART I



1,2,3,4 5,6,7,8 9,10,11,12

TABLE I

Physical Data for Polycyclic 2-Oxazolines and Their Hydrochloride Salts

C'mpd.	Yield, %	Mp, °C	Formula	% Calcd.				% Found			
				C	H	N	Cl	C	H	N	Cl
5	73	188-189	$C_{27}H_{19}NO$	86.83	5.14	3.75		87.07	5.00	3.58	
6	84	223-224	$C_{27}H_{19}NO$	86.83	5.14	3.75		86.92	5.23	3.58	
7	80	159-161	$C_{23}H_{17}NO$	85.41	5.31	4.33		85.54	5.14	4.14	
8	86	274-275	$C_{23}H_{17}NO$	85.41	5.31	4.33		85.35	5.24	4.28	
9	73	197-199	$C_{27}H_{20}ClNO$	79.10	4.93	3.42	8.65	79.27	5.11	3.35	8.81
10	84	203-205	$C_{27}H_{20}ClNO$	79.10	4.93	3.42	8.65	79.31	4.68	3.23	8.79
11	70	152-154	$C_{23}H_{18}ClNO$	76.76	5.05	3.89	9.85	76.82	5.07	3.74	9.61
12	86	199-201	$C_{23}H_{18}ClNO$	76.76	5.05	3.89	9.85	76.83	5.10	3.99	10.05

EXPERIMENTAL

The mps of all compounds were taken on a Fisher-Johns melting point block and are uncorrected. Analyses were performed by Galbraith Labs., Knoxville, Tennessee; M-H-W Labs., Garden City, Michigan; and on a departmental F and M Scientific Corp., Model 185, C, H, and N analyzer. The nmr spectra were recorded on a Varian A-60 spectrophotometer, using 10% deuterated chloroform solutions with tetramethylsilane (TMS) as an internal standard.

4-(7-Benz[a]anthracenyl)phenyl-2-oxazoline (6).

A mixture of 8.2 g (0.022 mole) of 2 and 20 g (0.13 mole) of powdered sodium iodide in 200 ml of THF was refluxed for 24 hrs with vigorous mechanical stirring. The solution was then concentrated, the residue dissolved in 100 ml of chloroform, 100 ml of water added, and the chloroform layer separated and dried over sodium sulfate. The dried solution was filtered and concentrated to give a viscous oil. The oil readily crystallized when 50 ml of ethanol (95%) was added. The solid was recrystallized four times from benzene-ethanol (95%) (1:1), and the product was obtained as white crystals, mp 223-224°; yield 7.5 g (84%); nmr ($CDCl_3$) δ 5.0-4.0 (m, 15, ArH), 2.4 (t, 2, CH_2), 2.2 (t, 2, CH_2).

3-(7-Benz[a]anthracenyl)phenyl-2-oxazoline (5).

Using the same procedure as described above, on the same scale with 1, produced a solid which was purified by three recrystallizations from benzene-ethanol (95%) (7:3) and one treatment with charcoal. This afforded 6 g (73%) of white crystals, mp 188-189°; nmr ($CDCl_3$) δ 5.0-4.0 (m, 15, ArH), 2.4 (t, 2, CH_2), 2.2 (t, 2, CH_2).

4-(9-Anthracenyl)phenyl-2-oxazoline (8).

Using the same procedure as described above with 9.17 g (0.03 mole) of 4 and 22 g (0.15 mole) of powdered sodium iodide, produced a solid which was purified by four recrystallizations from chloroform-ethanol

(95%) (4:6). The product was isolated as greenish yellow needles, mp 274-275°; yield 8.4 g (86%); nmr ($CDCl_3$) δ 4.6-4.0 (m, 13, ArH), 2.44 (t, 2, CH_2), 2.22 (t, 2, CH_2).

3-(9-Anthracenyl)phenyl-2-oxazoline (7).

Using 10 g (0.031 mole) of 3, 22 g (0.15 mole) of powdered sodium iodide and the same procedure as described above, produced, after concentration of the chloroform layer, a pale brown oil which crystallized on standing. Purification by four recrystallizations from THF-ethanol (95%) (7:3) and one treatment with charcoal, afforded 7.1 g (70%) of light yellowish white needles, mp 159-161°; nmr ($CDCl_3$) δ 4.6-4.0 (m, 13, ArH), 2.4 (t, 2, CH_2), 2.2 (t, 2, CH_2).

4-(7-Benz[a]anthracenyl)phenyl-2-oxazoline hydrochloride (10).

To 3 g (0.008 mole) of 6 in 150 ml of THF at room temperature was added 60 ml of anhydrous ether saturated with anhydrous hydrogen chloride. The mixture was stirred for 15 min, concentrated, the resultant white solid recrystallized four times from absolute ethanol, and the product was isolated as white powdery crystals, mp 203-205°; yield 2.8 g (84%).

3-(7-Benz[a]anthracenyl)phenyl-2-oxazoline hydrochloride (9).

Using the same procedure as above on the same scale with 5 produced an oil which slowly crystallized from ether-ethyl acetate (1:1) after cooling overnight. The resultant white solid was recrystallized four times from ethyl acetate-absolute ethanol-ether (2:7:1), and the product isolated as a white powdery solid, mp 197-199°; yield 2.5 g (73%).

4-(9-Anthracenyl)phenyl-2-oxazoline hydrochloride (12).

Using the same procedure as above on the same scale with 8 produced

a light green oil which crystallized when 50 ml of ethyl acetate was added. The solid was recrystallized four times from absolute ethanol, and the product was isolated as light yellow feathery crystals, mp 199-201°; yield 2.8 g (86%).

3-(9-Anthracenyl)phenyl-2-oxazoline hydrochloride (11).

To 2.5 g (0.0077 mole) of 7 in 150 ml of warm THF was added 25 ml of anhydrous ether saturated with anhydrous hydrogen chloride. The mixture was stirred for 15 min, concentrated, the resultant yellow oil was recrystallized four times from absolute ethanol, and the product isolated as greenish yellow nugget crystals, mp 152-154°; yield 1.8 g (70%).

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