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SYNTHESIS OF 3', 4'-DIHYDRONAPHTH-1', 2' : 5, 4-OXAZOLE AND ITS 2-ARYL DERIVATIVES

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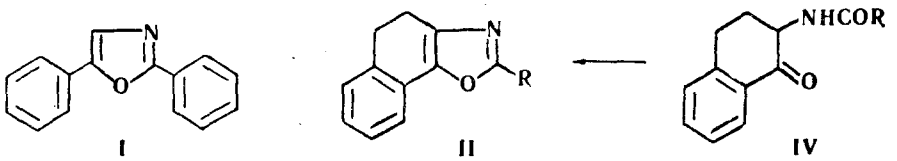
From 2-amino-1-keto-1, 2, 3, 4-tetrahydronaphthalene, prepared by reduction of isonitroso-α-tetralone, a number of N-acyl derivatives are prepared, and these are converted further to 2-substituted 3', 4'-dihydronaphth-1', 2':5, 4-oxazoles.

2-Aryl substituted 3', 4'-dihydronaphth-1', 2' : 5, 4-oxazoles are structural analogs of 2, 5-diphenyloxazole (I), which has found extensive application as a luminescent additive in liquid scintillators [1, 2]. We have now synthesized a number of 2-substituted 3', 4'-dihydronaphth-1', 2':5, 4-oxazoles (II), starting from 2-amino-1-keto-1, 2, 3, 4-tetrahydronaphthalene hydrochloride (III).

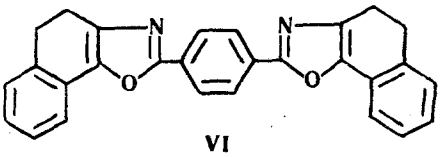
The hydrochloride III is prepared by reducing the isonitroso derivative of α-tetralone with zinc and acetic acid. This method is more convenient than those given in the literature [3-6]. N-Benzoyl-, N-p-tolyl-, N-p-phenylbenzoyl-2-amino-1-keto-1, 2, 3, 4-tetrahydronaphthalenes (IVc-d) were prepared by reacting the hydrochloride III with chlorides of aromatic carboxylic acids. The formyl derivative IVa is obtained by treating the hydrochloride III with orthoformic ester.



I II IV

a R=H; b R=CH_3; c R=C_6H_5; d R 2 p-$CH_3C_6H_4$; e R=p-$C_6H_5C_6H_4$.

Conversion of acyl derivatives IVa, c-e to 3', 4'-dihydronaphth-1', 2' : 5, 4-oxazole (IIa), 2-phenyl-, 2-p-tolyl-, and 2-p-diphenylyl-3', 4'-dihydronaphth-1', 2' : 5, 4-oxazoles (IIc-e) is effected by heating with phosphorus oxychloride. N, N'-Di(1-keto-1, 2, 3, 4-tetrahydronaphthyl-2) terephthaloyldiamide (V) was synthesized by treating the hydrochloride III with terephthaloyl dichloride, and further converted to 1, 4-di(3', 4'-dihydronaphth-1', 2' : 5, 4-oxazolyl-2) benzene (VI).



VI

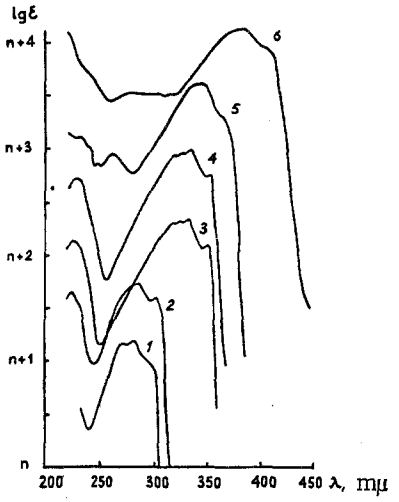
2-Methyl-3', 4'-dihydronaphth-1', 2' : 5, 4-oxazole (IIb) is obtained by heating the hydrochloride III with acetic anhydride, without isolating the acetyl derivative (IVb).

The figure gives the UV absorption spectra of the oxazoles IIa-e and VI synthesized, measured in cyclohexane using an SF-4 instrument. Comparison of the spectra of IIa-e and VI with those of the corresponding 2-substituted 5-phenyloxazoles [7, 8], shows that introduction of the CH_2-CH_2 group connecting the 5-phenyl and oxazole rings, gives rise to a rather strong bathochromic shift (20-30 mμ) of the long wave absorption. This shift is close in magnitude to that observed in the analogous transition from diphenyl to 9, 10-dihydrophenanthrene [9].

Experimental

2-Amino-1-keto-1, 2, 3, 4-tetrahydronaphthalene hydrochloride (III). 19 g (0.3 g at) Zn dust was added in small portions to a solution of 12 g (0.056 mole) K salt of the isonitroso derivative of α-tetralone [10] in 60 ml glacial acetic acid and 18 ml Ac_2O, with vigorous stirring, the temperature being 40°. After 30 min 60 ml water was added, and the

whole stirred for another 2 hr at 40°. The N-acetyl-2-amino-1-keto-1,2,3,4-tetrahydronaphthalene (IVb) isolated by extraction with $CHCl_3$ was refluxed for 1 hr with 30 ml concentrated HCl. The acid solution was diluted with an equal volume of water extracted with ether to remove impurities, and evaporated under reduced pressure. Yield of hydrochloride III, 5 g (0.025 mole), mp 189-192°. The literature gives two melting points, 117° [3], and 201-202° [4].



UV spectra of 3',4'-dihydronaphth-1',2':5,4-oxazoles. 1) 3',4'-Dihydronaphth-1',2':5,4-oxazole (IIa, n = 3.0); 2) 2-methyl-3',4'-dihydronaphth-1',2':5,4-oxazole (IIb, n = 2.5); 3) 2-phenyl-3',4'-dihydronaphth-, 1',2':5,4-oxazole (IIc, n = 2.0); 4) 2-p-tolyl-3',4'-dihydronaphth-1',2':5,4-oxazole (IId, n = 1.5); 5) 2-p-diphenylyl-3',4'-dihydronaphth-1',2':5,4-oxazole (IIe, n = 1.0); 6) 1,4-di(3',4'-dihydronaphth-1',2':5,4-oxazolyl-2) benzene (VI, n = 0.5).

N-Acyl derivatives of 2-amino-1-keto-1,2,3,4-tetrahydronaphthalene (IV and V). 1.6 g (19.5 mmole) fused NaOAc, 20 mmole aromatic carboxylic acid chloride, and an additional 1.6 g (19.5 mmole) NaOAc were added in succession to a hot solution of 17 mmole hydrochloride III in 60 ml glacial acetic acid. The suspension was agitated for 15 min at 100°, then poured into a solution of alkali. Yields of IVc-e, 40-70%.

Physical Constants and Analytical Data for the Compounds Prepared

Compound	Mp, °C (solvent)	Formula	Found, %			Calculated, %		
			C	H	N	C	H	N
IVa	117.0—118.0 heptane	$C_{11}H_{11}NO_2$	70.2 70.4	6.21 6.01	7.74 7.90	70.0	5.80	7.40
IVb	124.5—125.5* (H_2O)	$C_{12}H_{13}NO_2$			7.05 7.26			6.94
IVc	141.0—142.0 heptane	$C_{17}H_{15}NO_2$	77.1 77.2	5.79 5.65	5.38 5.22	77.0	5.66	5.28
IVd	149.0—150.0 aqueous EtOH	$C_{18}H_{17}NO_2$	77.5 77.5	6.33 6.43	4.90 4.96	77.5	6.13	5.02
IVe	146.0—147.0 aqueous EtOH	$C_{23}H_{19}NO_2$	80.7 80.8	5.67 5.83	3.95 4.18	81.1	5.64	4.11
V	223—225 aqueous EtOH	$C_{28}H_{24}N_2O_4$			6.17 6.58			6.22
IIa	39.0—40.0**	$C_{11}H_9NO$	77.0 77.4	5.22 5.38	8.19 8.47	77.2	5.32	8.18
IIb	bp 114° (2 mm)	$C_{12}H_{11}NO$	77.6 77.8	6.02 6.05	7.65 7.79	77.9	5.94	7.57
IIc	94.0—95.0 aqueous EtOH	$C_{17}H_{13}NO$	82.7 83.2	5.75 5.76	5.80 5.92	82.7	5.26	5.66
IId	109.0—110.0 aqueous EtOH	$C_{18}H_{15}NO$	82.8 82.8	6.11 5.90	5.40 5.39	82.8	5.79	5.36
IIe	129.0—130.0 aqueous EtOH	$C_{23}H_{17}NO$	85.4 85.2	5.56 5.40	4.46 4.65	85.5	5.27	4.34
VI	300—302 pyridine	$C_{28}H_{20}N_2O_2$	80.2 80.2	4.90 4.92	6.88 7.20	80.7	4.83	6.72

*Mp 127-128° is given in [5].

**Purified by vacuum-sublimation.

To prepare IVa, 1 g hydrochloride III was refluxed for 4 hr with 9 ml orthoformic ester, the excess of the latter distilled off under reduced pressure, the residue washed with benzene, and pressed on a porous tile, yield, 0.5 g.

2-Substituted 3', 4'-dihydronaphth-1', 2': 5,4-oxazoles (IIa-e, and VI). 5 mmole N-acyl derivative of 2-amino-1-keto-1,2,3,4-tetrahydronaphthalene was refluxed for 8 hr with 40 ml $POCl_3$. Most of the latter was then distilled off under reduced pressure, and the residue poured into water. The oxazole which separated was extracted with ether, precipitated as hydrochloride, and then converted to free base. Yields of oxazoles, 30-50%.

To prepare the oxazole IIb, 3.6 g (18 mmole) hydrochloride III was refluxed for 5 hr with 24 ml Ac_2O. Excess of the latter was distilled off, and the residue distilled under reduced pressure. The oxazole obtained was purified by conversion to the hydrochloride, mp 158.5°-163.5°, yield 1.7 g (9.2 mmole). Found: Cl 15, 8, 15.7; N 6.22, 6.69%. Calculated for $C_{12}H_{12}ClNO$: Cl 16.0; N 6.27%.

REFERENCES

1. Liquid Scintillation Counting, ed. C. G. Bell and F. N. Hayes, Pergamon, 101, 1958.
2. V. O. Vyazemskii, I. I. Lomonosov, A. N. Pisarevskii, Kh. V. Protopopov, V. A. Ruzin, and E. D. Teterin, Scintillation Methods in Radiometry [in Russian], Gosatomizdat, Moscow, 68, 1961.
3. P. V. Neber, A. Burgard, and W. Thier, Ann., 526, 277, 1936.
4. H. E. Baumgarten and I. M. Petersen, J. Am. Chem. Soc., 82, 459, 1960.
5. E. Chiorenesku and L. Bukhen-Byrlendyanu, Izv. AN SSSR, OKhN, 169, 1961.
6. C. O'Brien, Chem. Rev., 64, 81, 1964.
7. H. Bredereck, R. Compper, and F. Reich, Ber., 93, 1389, 1960.
8. D. G. Ott, F. N. Hayes, E. Hausburey, and V. N. Kerr, J. Am. Chem. Soc., 79, 5448, 1957.
9. W. Klyne and P. B. D. de la Mare, Progress in Stereochemistry, vol. 2 [Russian translation], Goshkhimizdat, Moscow, 349, 1961.
10. F. Straus, Ann., 444, 162, 1925.

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SYNTHESIS OF 4- AND 8-METHYLTHIENOTHIENOPYRIDINES

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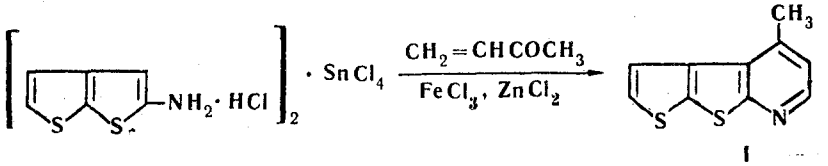
The synthesis of some new heterocyclic bases is described. These are 4-methylthieno(2,3-b) thieno (2,3-b)-pyridine (I), and 8-methylthieno(3,2-b) thieno(2,3-b) pyridine (II).

We have previously obtained 4- and 7-methylthieno- and 1-methylthionaphthenopyridine [1,2]. The present communication describes the synthesis of new heterocyclic bases, 4, -methylthieno [2,3-b]-thieno [2,3-b]-(I) and 8-methylthieno [3,2-b] thieno [2,3-b] pyridine (II).

Compound I was synthesized by a somewhat modified Doebner-Miller synthesis, by reacting methylvinylketone with the stannic chloride double salt of 2-aminothieno [2,3-b] thiophene hydrochloride in the presence of ferric chloride plus anhydrous zinc chloride in ethanol solution, heat being used [3].



I

The isomeric base II is obtained by the same method, starting from the stannic chloride double salt with 2-amino-thieno [3,2-b] thiophene hydrochloride [3].