320 nm, ε 5.5-10³ [2]). This fact becomes understandable if one considers that, according to the data in [2], the phenyl substituent in 4-phenylpyrimido[1,2-a]benzimidazoles is virtually perpendicular to the plane of the heteroring, while this sort of orientation is impossible in VII because of the presence of an annelated six-membered carbocycle.

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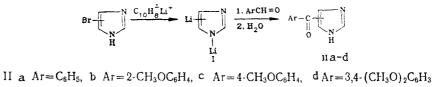
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SYNTHESIS OF ARYL 4(5)-IMIDAZOLYL KETONES

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It is known that arylhetarylcarbinols are formed in the reaction of active organometallic compounds of N-substituted azoles (with N-alkyl, N-aralkyl, and N-aryl substituents) with aromatic aldehydes [1, 2]. However, instead of the expected aryl[4(5)-imidazolyl]carbinols, we obtained aryl 4(5)-imidazolyl ketones IIa-d by the action of aromatic aldehydes on imidazolyl-1,4(5)-dilithium, formed from 4(5)-bromoimidazole and naphthyllithium.

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This pathway for obtaining ketones II gives better results than the synthesis of the ketones by the known reaction of organolithium compounds with carboxylic acid nitriles.

A solution of 1.1 g (7.5 mmole) of 4(5)-bromoimidazole in 10 ml of THF was added in the course of 5 min with stirring in an argon atmosphere at -10° C to -15° C to naphthyllithium obtained from 0.21 g (30 mmole) of finely ground lithium and 3.84 g (30 mmole) of naphthalene in 20 ml of THF, 5 min after which a solution of 35 mmole of the aromatic aldehyde in 10 ml of THF was added, and the mixture was maintained at -10° C to -15° C for 30 min and at 20-25°C for 2 h. The usual workup gave aryl 4(5)-imidazolyl ketones IIa-d in 48-63% yields.

Ketones IIa and IIc are formed in 17% and 24% yields, respectively, when the aromatic aldehydes are replaced by benzonitrile and p-methoxybenzonitrile.

Phenyl 4(5)-Imidazolyl Ketone (IIa). This compound had mp 149-150°C (from aqueous alcohol). IR spectrum (CHCl₃): 1640 (C=O), 3440 cm⁻¹ (NH). PMR spectrum (CF₃COOH): 7.25 (5H, m, C₆H₅): 7.70 [1H, s, 4(5)-H], 8.54 ppm (1H, m, 2-H). The yield was 55%.

2-Methoxyphenyl 4(5)-Imidazolyl Ketone (IIb). This compound had mp 129-130°C (from ethyl acetate). IR spectrum (CHCl₃): 1642 (C=O), 3448 cm⁻¹ (NH). PMR spectrum (CF₃COOH): 3.38 (3H, s, OCH₃), 6.87 (4H, m, C₆H₄), 7.50 [1H, s, 4(5)-H], 8.42 ppm (1H, m, 2-H). The yield was 52%.

4-Methoxyphenyl 4(5)-Imidazolyl Ketone (IIc). This compound had mp 191-192°C (from alcohol). IR spectrum (CHCl₃): 1633 (C=O), 3438 cm⁻¹ (NH). PMR spectrum (CF₃COOH): 3.52 (3H, s, OCH₃), 6.71 (2H, d, J = 9.45 Hz, C₆H₄), 7.58 (2H, d, J = 9.45 Hz, C₆H₄), 7.72 [1H, s, 4(5)-H], 8.57 ppm (1H, m, 2-H). The yield was 48%.

3,4-Dimethoxyphenyl 4(5)-Imidazolyl Ketone (IId). This compound had mp 208-209°C (from alcohol). IR spectrum (CHCl₃): 1630 (C=O), 3432 cm⁻¹ (NH). PMR spectrum (CF₃COOH): 3.57 (6H, s, two OCH₃ groups), 6.70 (1H, d, J = 9.45 Hz, C₆H₃), 7.20 (1H, s, C₆H₃), 7.33 (1H, d, J = 9.45 Hz, C₆H₃), 7.75 [1H, s, 4(5)-H], 8.57 ppm (1H, m, 2-H). The yield was 63%.

The results of elementary analysis of ketones IIa-d were in agreement with the calculated values.

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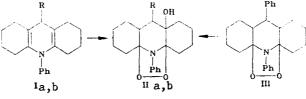
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HYDROXYPEROXIDATION OF 1,2,3,4,5,6,7,8,9,10-DECAHYDROACRIDINE DERIVATIVES

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In the case of 9-R-10-phenyldecahydroacridines Ia, b we have for the first time accomplished the hydroxyperoxidation of 1,4-dihydropyridine derivatives: peroxy and hydroxy groups are simultaneously introduced into the hydropyridine ring by treatment of Ia, b with a mixture of hydrogen peroxide and peracetic acid or, better yet, peroxymonophthalic acid in the presence of HCl. Compound IIa was obtained under similar conditions from epidioxyperhydroacridine derivative III.



I, II a $R = C_6H_5$, b $R = CH_2C_6H_5$

Compound IIa. This compound had mp 175-177°C (from ethyl acetate). IR spectrum (in CHCl₃): 3576 cm⁻¹ (OH). PMR spectrum (in CDCl₃): 3.20 (1H, d, J = 11 Hz, 9-H), 2.31 ppm (1H, m, J = 11 and 3.5 Hz, 9a-H). Mass spectrum (70 eV), m/z (I_{rel} , %): 391 (29), M⁺; 373 (42), [M – H₂O]⁺; 359 (100), [M – O₂]⁺; 357 (88), [M – H₂O₂]⁺; 341 (33), [M – O₂ – H₂O]⁺. The yield was 51% (from Ia).

Compound IIb. This compound had mp 168-170°C (from ethyl acetate). IR spectrum (in CHCl₃): 3560 cm⁻¹ (OH). Mass spectrum (70 eV), m/z (I_{rel}, %): 405 (12), M⁺; 387 (35), $[M - H_2O]^+$; 373 (100), $[M - O_2]^+$; 356 (80), $[M - O_2 - H_2O]^+$. The yield was 79%.

The results of elementary analysis of IIa, b were in agreement with the calculated values.

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