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THE SYNTHESIS OF NAPHTH[2,1-a]- AND NAPHTH[2,3-a]AZULENES[1)]

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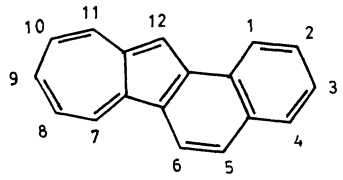
Naphth[2,1-a]- and naphth[2,3-a]azulenes were synthesized by dehydrogenation of 5,6-dihydronaphth[2,1-a]- and 5,12-dihydronaphth[2,3-a]azulenes which were obtained by the reaction of 2H-cyclohepta[b]furan-2-one with 1- and 2-pyrrolidinyl-3,4-dihydronaphthalenes, respectively.

The polycyclic aromatic hydrocarbons which consist of the azulene ring condensed with benzenoid aromatics are interest in their physical properties and physiological activities,[2)] as well as the chemical behaviors. Among of these compounds, naphth[a]azulenes, such as naphth[2,1-a]- (1) and naphth[2,3-a]azulenes (2), are fundamental compounds as higher benzologs of benz[a]azulene,[3)] but any



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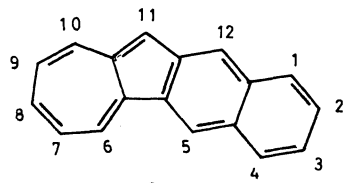

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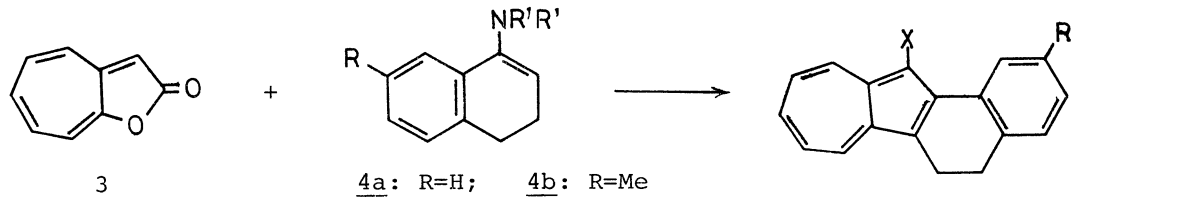
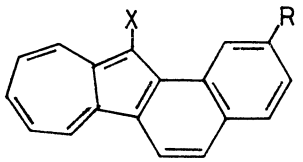
isomer of naphth[a]azulene has not yet been synthesized. The present authors have previously reported the useful method for synthesizing the azulene ring utilizing the reaction of 2H-cyclohepta[b]furan-2-one (3) with enamines[4)] and the reaction has been applied on the facile synthesis of indenoazulenes.[5)] This communication describes the synthesis of 1 and 2 from 3 *via* dihydronaphth[a]azulenes which were obtained by the reaction of 3 with the enamines of α- and β-tetralones, that is, 1- (4a, b, c)[6)] and 2-pyrrolidinyl-3,4-dihydronaphthalenes (5).[7)]

The Synthesis of Naphth[2,1-a]azulene (1a) and Its 2-Methyl and 2-t-Butyl Derivatives (1b and 1c). A solution of 3 and 2 molar equivalents of 4a in



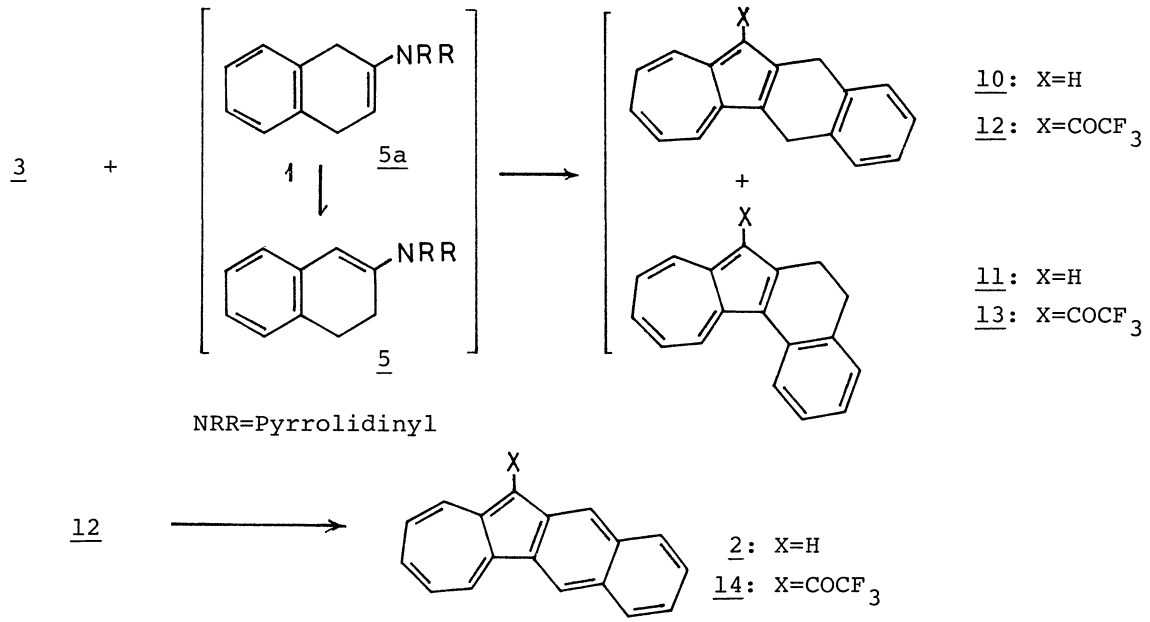
3 + 4a: R=H; 4b: R=Me
4c: R=t-Bu
NR'R'=Pyrrolidinyl

6a: R=X=H; 6b: R=Me, X=H
6c: R=t-Bu, X=H
7: R=H, X=$COCF_3$
8: R=H, X=CO_2Me



1a: R=X=H
1b: R=Me, X=H
1c: R=t-Bu, X=H
9: R=H, X=CO_2Me

anhydrous ethanol was heated under reflux for 4 hr. At that time, one more molar equivalent of 4a was added and the heating was continued for an additional 4 hr. After evaporation of the solvent, the residue was chromatographed (silica gel, benzene-cyclohexane). The bluish fraction afforded 5,6-dihydronaphth[2,1-a]-azulene (6a) [blue scales, mp 169-170°C][8] in a 50% yield. In a similar manner, the reaction of 3 with 7-methyl (4b) and 7-t-butyl derivatives (4c) of 4a yielded 2-methyl (6b) [blue scales, mp 156-157°C] and 2-t-butyl derivatives (6c) [bluish green needles, mp 142°C] of 6a in 45 and 38% yields, respectively. On heating in p-cymene in the presence of 5% Pd-C, 6a, b, c resulted in dehydrogenation to give 1a [green scales, mp 253-254.5°C], 1b [green scales, mp 200-201°C] and 1c [green scales, mp 180-181°C] in 52, 50, and 55% yields, respectively. The dehydrogenation of 6a, b, c with one molar equivalent of DDQ in benzene also yielded 1a, b, and c in 68, 65, and 68% yields, respectively. Further, the dehydrogenation of 6a into 1a was achieved in a satisfactory yield as follows: A trifluoroacetyl derivative (7) [brown oil], derived from 6a by treatment with $(CF_3CO)_2O$, was hydrolyzed with aq. NaOH in ethanol, and the subsequent methylation of the resulting carboxylic acid with diazomethane gave an ester (8) [violet oil] in an 85% yield from 6a. The dehydrogenation of 8 with DDQ in benzene yielded methyl naphth[2,1-a]azulene-12-carboxylate (9) [green needles, mp 120-121°C] in an almost quantitative yield. On heating with 100% phosphoric acid, 9 resulted in demethoxycarbonylation to give 1a in an almost quantitative yield. The spectral data of 1a, b, and c were shown in Table 1.



The Synthesis of Naphth[2,3-a]azulene (2). A solution of 3 and 3 molar equivalents of the enamine, 5, in anhydrous ethanol was heated under reflux for 462 hr. After evaporation of the solvent, the residue was chromatographed (silica gel, benzene-cyclohexane) and the bluish fraction was recrystallized from benzene to give 5,12-dihydronaphth[2,3-a]azulene (10) [blue scales, mp 207-209°C, pmr ($CDCl_3$) δ 4.50 ppm (4H, s, CH_2)] in a 20% yield. An expected 5,6-dihydronaphth[1,2-a]-azulene (11) could not be isolated. However, the trifluoroacetylation of mother liquor of the recrystallization yielded 7-trifluoroacetyl-5,6-dihydronaphth-[1,2-a]azulene (13) [brown oil, pmr ($CDCl_3$): δ 3.33 (2H, t, J = 7.0 Hz, CH_2) and 3.85 ppm (2H, t, J = 7.0 Hz, CH_2)] as a minor product, as well as 11-trifluoro-acetyl-5,12-dihydronaphth[2,3-a]azulene (12) [brown oil, pmr($CDCl_3$): δ 4.27 (2H, br. s, CH_2) and 4.57 ppm (2H, br. s, CH_2)] which was derived from 10 by treatment with $(CF_3CO)_2O$. The structures of 12 and 13 were established on the basis of their pmr spectral data. The enamine (5) is known to react with electrophiles not only at the 1-position, but also at the 3-position, in spite of the minor contribution of a tautomer (5a).[7] In the case of 3, the reaction took place more easily with 5a rather than 5, giving mainly 10.

The treatment of 12 with DDQ resulted in an easy dehydrogenation to give 11-trifluoroacetylnaphth[2,3-a]azulene (14) [brownish violet needles, mp 177.5-178°C] in a quantitative yield. The hydrolysis of 14 with aq. NaOH in ethanol and the subsequent decarboxylation of the resulting carboxylic acid with 100% phosphoric

acid yielded 2 [green scales, mp 223-224°C] in an almost quantitative yield. Naphth[1,2-a]azulene could not be synthesized because of a low yield of 13. The spectral data of 2 were shown in Table 1.

Table 1. The UV and IR spectral data of naphth[a]azulenes, 1a, 1b, 1c, 9, and 2.

	UV in MeOH, λmax nm (log ε)	IR (KBr) cm^{-1}
1a	272 (4.24), 322 (4.87), 375 (3.92) 395 (3.54), 411 (3.17), 580 (2.46) 630 (2.57)	1570, 1460, 1442, 1280, 1190 932, 800, 742, 721, 705
1b	270 (3.89), 316 (4.54), 326 (4.59) 374 (3.89), 395 (3.91), 599 (2.00) 638 (2.08)	1570, 1530, 1475, 1380, 1290 1205, 938, 880, 750, 735
1c	270 (3.90), 315 (4.51), 327 (4.56) 375 (3.90), 396 (3.93), 580 (2.46) 640 (2.55)	1592, 1578, 1470, 1373, 1285 1180, 1015, 935, 880, 830
9	270 (4.21), 278 (4.21), 319 (4.20) 355 (4.24), 396 (3.91), 618 (2.57)	1685, 1595, 1580, 1455, 1410 1402, 1220, 1210, 1195, 1130 1100, 800, 750, 745
2	269 (4.41), 279 (4.38), 316 (4.77) 326 (4.76), 366 (3.85), 392 (3.72) 414 (3.66), 586 (2.52), 647 (2.60)	1620, 1586, 1490, 1466, 1402 1392, 1330, 1304, 1262, 1238 1205, 1110, 1006, 946, 920 878, 810, 723, 668

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References and Notes

1) Part III of the series of the syntheses of azulene derivatives by the reactions of 2H-cyclohepta[b]furan-2-one with enamines. Part II see ref. 5).
2) a) D. J. Bertelli and P. Crews, Tetrahedron, 26, 4717 (1970), b) C. Jutz, E. Schweger, Hans-Goerg Lovering, A. Kraatz, and W. Kosban, Chem. Ber., 107, 2956 (1974), c) N. P. Buu-Hoi, D. P. Hien, C. Jutz, Naturwissenschaften, 54, 420 (1967); N. P. Buu-Hoi, N. B. Ciao, C. Jutz, ibid., 57, 499 (1970).
3) Pl. A. Plattner, A. Furst, J. Chopin, and G. Winteler, Helv. Chem. Acta, 31, 501 (1948); W. Treibs, Chem. Ber., 81, 381 (1948).
4) P. W. Yang, M. Yasunami, and K. Takase, Tetrahedron Lett., 1971, 4725.
5) Alice Chen, M. Yasunami, and K. Takase, Tetrahedron Lett., 1974, 2581.
6) L. H. Hellberg, R. J. Milligan, and R. N. Wilke, J. Chem. Soc. (C) 1970, 2581.
7) G. Pitacco, F. Paolo Colonna, E. Valentin, and A. Risaliti, J. Chem. Soc. Perkin I, 1974, 1625.
8) All new crystalline compounds gave satisfactory results of elementary analyses in accord with the assigned structures.

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