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7,10,14-TRI-*t*-BUTYL-3-AMINO-1,8-BISDEHYDRO[14]ANNULENE

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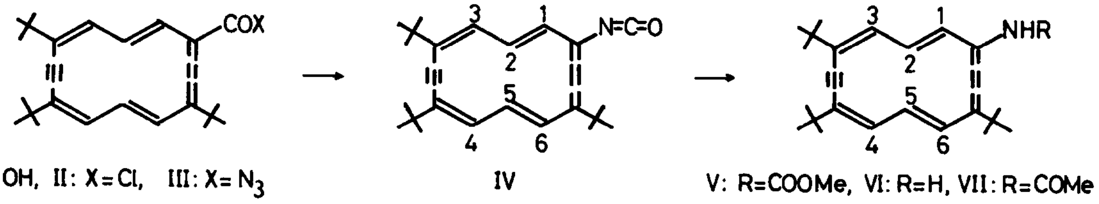
Summary: Tri-*t*-butylcarboxybisdehydro[14]annulene was converted by the Curtius reaction into unstable aminoannulene, which could be characterized as N-acetyl derivative. The pK$_a$-value of the aminoannulene reflects aromatic nature of the annulene nucleus.

Aminoannulenes are interesting compounds being formal counterpart of aniline. However, little is known hitherto on amino derivative of annulene.1,2) Because we have previously prepared 7,10,14-tri-*t*-butyl-3-carboxy-1,8-bisdehydro[14]annulene (I),3) transformation of the carboxyl group in amino seemed to be of considerable interest.

Acid chloride (II, a viscous reddish violet liquid) was obtained on treatment of I with thionyl chloride in dichloromethane. The reaction of II with sodium azide in an aqueous acetone yielded a stable acid azide (III, dark red crystals, mp 131.1-133.3°C, Mass(m/e): 415 (M^+), 387 (M^+-28); NMR($CDCl_3$): τ 0.07 (1H, d, J=13.5, H^1), 0.47, 0.65, 0.68 (each 1H, d, J=13.5, H^3, H^4, H^6), 8.08, 8.10, 8.12 (each 9H, s, *t*-Bu), 13.97 (1H, t, J=13.5, H^5), 14.24 (1H, t, J=13.5, H^2)) in a high yield (94%).4) Since it is well-known that aromatic acid azides are much more stable than aliphatic ones, the high stability of III seems to be ascribable to the aromatic nature of the annulene nucleus. A benzene solution of III was refluxed for 2.5 hrs. to give isocyanate (IV, a viscous red liquid), which was treated with potassium hydroxide in methanol at room temperature to give methyl urethane (V, orange crystals, mp 140-143°C (dec.), 76%, Mass(m/e): 419 (M^+), 404 (M^+-15); IR(KBr-disk): 3290 m, 2960 s, 2100 w, 2030 w, 1715 s, 1390 w, 1360 m, 1235 s, 1067 s, 963 m cm^{-1} ; UV(λ_{max}^{THF} nm (ε)): 307.5 sh (26100), 337.5 (164000), 470 (22300), 532 (400), 553 (500), 598 (1800)). As attempted hydrolysis of V to obtain aminoannulene (VI) resulted in a fatal decomposition, 1M aqueous solution of sodium hydroxide was added at room temperature to a stirred acetone solution of the isocyanate (IV). After 5 min., the reaction mixture was neutralized with 1N sulphuric acid1) and worked up in the usual manner. The aminoannulene (VI, a greenish red solid, mp 150°C (dec.); NMR($CDCl_3$): τ 0.76 (1H, d, J=14.0, H^4), 0.78 (1H, d, J=14.0, H^6), 1.00 (1H, d, J=14.0, H^3), 1.34 (1H, d, J=14.0, H^1), 5.15 (2H, br. s, NH_2), 8.15 (18H, s, *t*-Bu × 2), 8.19 (9H, s, *t*-Bu), 14.12 (1H, t, J=14.0, H^2), 14.15 (1H, t, J=14.0, H^5); UV(λ_{max}^{THF} nm (ε)): 268.5



I: X=OH, II: X=Cl, III: X=N_3

IV

V: R=COOMe, VI: R=H, VII: R=COMe

(10200), 285.5 sh (10600), 337 (65100), 351 sh (53700), 495 (12900), 544 (2100), 566 (2000), 612 (8600)) thus obtained was found to be sensitive to atmospheric oxygen. The reaction of acetic anhydride with VI in ether yielded stable N-acetylaminoannulene (VII, orange yellow needles, mp 207-210°C (dec.); Mass(m/e): 403 (M^+), 388 (M^+-15); NMR($CDCl_3$): τ 0.67 (1H, d, J=13.5), 0.70 (3H, d, J=13.5), 1.92 (1H, br. s, NH), 7.53 (3H, s, CH_3), 8.12 (9H, s, *t*-Bu), 8.13 (18H, s, *t*-Bu × 2), 14.43 (1H, t, J=13.5), 14.47 (1H, t, J=13.5); UV(λ_{max}^{THF} nm (ε)): 305 sh (26500), 329 sh (82700), 339.5 (174000), 472.5 (15200), 532 (340), 554 (480), 599 (1500)).

The pK_a'-value for VI could be determined by a spectrophotometric method in ethanol-water system (1:1) using phosphate-borate buffer solution. Change of absorbance at 495 nm was measured at 0°C to minimize the decomposition of VI. The pK_a'-values of aniline and *p*-*t*-butylaniline were also determined under the same conditions. As shown in Table, the pK_a'-values obtained for aniline and *p*-*t*-butylaniline are in good agreement with the reported values.[5] The observed pK_a'-value for the amino[14]annulene (VI, 3.05 ± 0.16) is smaller than those for condensed aromatic 14π-electron system such as 1-amino (3.53), 9-aminophenanthrene (3.49) and 1-aminoanthracene (3.50), and is approaching to that for 3-aminopyrene (3.12).[8] Because it is known that the basisity of aromatic amine decreases with the augmentation of π-electron system, the result obtained indicates that the bisdehydro[14]annulene nucleus has even higher ability to delocalize unshared electron pair on amino nitrogen atom over the nucleus than condensed aromatic nuclei containing 14π electrons.

Table. pK_a'-values at 0°C

amine	pK_a'	pK_a (lit.)
amino[14]annulene	3.05 ± 0.16	
aniline	4.50 ± 0.09	4.54
p-*t*-butylaniline	4.92 ± 0.14	4.93

References and Notes

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4) All new crystalline compounds reported in this communication gave satisfactory elemental analyses.
5) The reported pK_a-values for aniline (4.26) and *p*-*t*-butylaniline (4.62) at 25°C in ethanol-water (1:1)[6] were converted to the values at 0°C using the equation proposed by Perrin ($-d(pK_a)/dT = (pK_a - 0.9)/T$).[7]
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