THE SYNTHESIS AND CHEMICAL PROPERTIES OF 11H-CYCLOHEPT[b]INDENO[2,1-d]PYRROLE[1]

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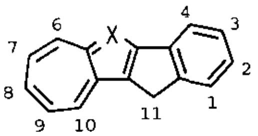
Abstract——The reaction of N-(3-indenyl)iminotributylphosphorane with 2-chlorotropone gave novel 11H-cyclohept[b]indeno[2,1-d]pyrrole, which was converted to the corresponding ketone and alcohol. The chemical properties of the three compounds were studied.

Azaazulenes[2] have received considerable interest, particularly in comparison with the chemistry of azulenes, and have played a major role in the advancement of our understanding of cyclic conjugation.[3] The tetracyclic system containing the 1-azaazulene nucleus, 11H-cyclohept[b]indeno[2,1-d]pyrrole (1) is of interest as a precursor of fully conjugated systems such as an anion (A) (18 π electron system) and a cation (B) (16 π electron system). The synthesis of 11H-indeno[2,1-a]-azulene (2), which is a carbocyclic analogue of 1, has been accomplished previously.[4,5] Although the methodology constructing azulenes condensed with several ring systems has been reported,[6] no convenient synthesis of 1-azaazulenes condensed with various ring systems has been explored. Previously, the present authors have found that the reaction of 2-chlorotropone with N-vinylimino-phosphoranes resulted in the formation of 1-azaazulenes[7] in a single step. This communication will describe a simple preparation and chemical properties of 1. Our synthetic strategy was at first to obtain N-(3-indenyl)iminotributylphosphorane (4). The compound 4 [8,9] was easily prepared by the Staudinger reaction[10] of 3-azidoindene (3)[11] with tributylphosphine in anhydrous



1: X = N; 2: X = CH

(A): * = -; (B): * = +

benzene at room temperature for 1 h. Since the compound 4 was not stable and hydrolyzed to give 1-indanone under workup conditions,[7,12] the synthetic reaction was carried out conveniently in one-pot procedure without isolation of 4. When a solution of 3 (3 mmol) and tributylphosphine (3 mmol) in anhydrous benzene (35 ml) was stirred at room temperature, the reaction proceeded easily with the complete disappearance of 3 within 1 h. To this reaction mixture was added 2-chlorotropone (3 mmol) and triethylamine (3 mmol), and the mixture was heated under reflux for 3 h. The product was then separated through column chromatography on alumina by using chloroform-ethyl acetate (4/1) as eluent to give 1 as reddish purple needles (from ethanol), mp 184-185 °C, in a 64% yield. The plausible reaction pathways are shown in Scheme 1.[7,12] The initial step is an enamine type alkylation of 4 onto 2-chlorotropone followed by the hydrogen migration to give the intermediate 5. Then the intramolecular aza-Wittig reaction of 5 gives 6, which undergoes the dehydrochlorination to give 1. On treatment of 1 with potassium t-butoxide in MeOD at 0 °C, the methylene hydrogens of 1 was exchanged with deuterium to give 7 in a 60% yield after purification by tlc. Thus, the formation of an anion, which is formally isoelectronic to (A), was indicated. On the other hand, the treatment

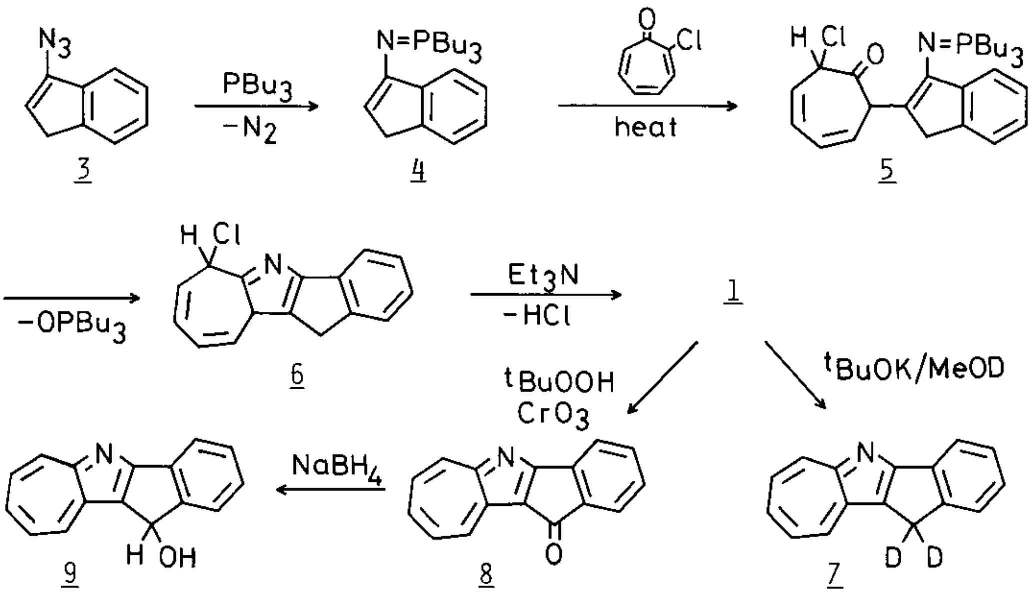
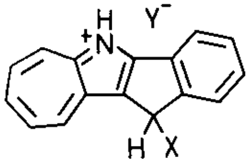
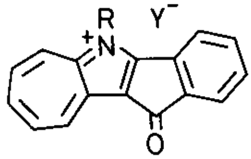


Table 1. The uv and ^{1}H-nmr spectral data of 1, 8, and 9

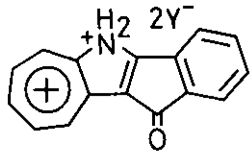
	1	8	9
λ_{max} (log ε)			
in EtOH	292 (4.46), 312 (4.32), 324 (4.40), 351 (3.84), 369 (3.81), 490 (3.44), 514 (3.41), 553 (sh, 3.03)	260 (4.05), 312 (4.71), 353 (3.98), 427 (3.37), 455 (3.45), 477 (3.42), 505 (sh, 3.14)	291 (4.53), 307 (4.48), 321 (4.55), 351 (3.89), 369 (3.86), 485 (3.58), 506 (3.56), 543 (sh, 3.23)
in 10% H_2SO_4	285 (sh, 4.42), 308 (4.62), 458 (4.15), 502 (sh, 3.79)	259 (4.29), 302 (4.79), 431 (3.99), 452 (3.99), 482 (sh, 3.67)	284 (sh, 4.27), 307 (4.46), 459 (4.11), 502 (sh, 3.64)
in conc. H_2SO_4	305 (4.70), 440 (sh, 4.08), 459 (4.15), 485 (sh, 3.92)	262 (4.57), 303 (4.30), 366 (3.97), 410 (sh, 3.61), 435 (3.46)	309 (4.48), 448 (sh, 4.09), 464 (4.12), 496 (sh, 3.83)
δ (ppm)			
in $CDCl_3$	3.90 (2H, s, H-11), 7.30-7.75 (6H, m, H-1,2,3,7,8,9), 8.07-8.20 (1H, m, H-4), 8.20-8.39 (1H, d, J= 9.2 Hz, H-10), 8.50-8.67 (1H, m, H-6)	7.26-7.48 (2H, m, H-2,3) 7.50-7.78 (5H, m, H-1,4,7,8,9) 8.42-8.66 (2H, m, H-6,10),	5.60-6.18 (2H, br, H-11 and hydroxyl), 7.33-7.52 (2H, m, H-2,3), 7.55-7.93 (5H, m, H-1,4,7,8,9), 8.38-8.63 (2H, m, H-6,10)
in $CDCl_3$-CF_3CO_2H	4.08 (2H, s, H-11), 7.30-7.81 (3H, m, H-1,2,3), 7.81-8.36 (4H, m, H-4,7,8,9), 8.58-8.98 (2H, m, H-6,10)	7.48-7.96 (4H, m, H-1,2,3,4), 8.16-8.50 (3H, m, H-7,8,9) 8.96-9.22 (2H, m, H-6,10),	5.96 (1H, s, H-11), 7.54-8.04 (4H, m), H-1,2,3,4), 8.26-8.55 (3H, m, H-7,8,9), 8.92-9.18 (2H, m, H-6,10)



10 : X=H
11 : X=OH



12 : R=H , Y=HSO_4
13 : R=Me, Y=I



14 : Y=HSO_4

of 1 dissolved in dichloromethane with catalytic amount of chromium trioxide and t-butyl hydroperoxide[13] afforded 11H-cyclohept[b]indeno[2,1-d]pyrrol-11-one (8)[8] as orange needles (from ethanol), mp 203-204 °C, in a 79% yield. On treatment with sodium borohydride in methanol, 8 was reduced to give 11-hydroxy-11H-cyclohept[b]indeno[2,1-d]pyrrole (9)[8] as red needles (from ethanol), mp 178-179 ° C, in a 47% yield.

The ^{1}H-nmr and uv spectral data of 1, 8, and 9 are appropriate for their structures (Table 1). The compound 1 gave 10 (Y=BF_4)[8,14] in 94% yield on treatment with tetrafluoroboric acid. The uv spectra of 1 in 10% and conc. sulfuric acid are almost identical with that of 10 (Y=BF_4) in acetonitrile. This finding and the ^{1}H-nmr spectrum of 1 in $CDCl_3$-CF_3CO_2H, showing a downfield shift of all the signals, indicate that 1 exists in a protonated azaazulenium ion 10 in acidic media. The spectral properties of 9, showing a similarity to those of 1, imply the existence of 11 in acidic media. The protonation occurs at the nitrogen atom, and no dehydroxylation leading to (B) (16π electron system) took place even in conc. sulfuric acid. In addition, the spectral properties of 8 in acidic media exhibited a similar behavior to those of 1 and 9. The uv spectrum of 8 in 10% sulfuric acid is very similar to that of 13.[15] These findings indicate that 8 exists in a structure 12, protonated at the nitrogen atom, but not at the carbonyl oxygen. However, the uv spectrum of 8 in conc. sulfuric acid is markedly different from those in ethanol or 10% sulfuric acid, and it is similar to that of 2-phenyl-1-indenone.[16] This fact suggests that 8 is doubly protonataed at the nitrogen atom, but not at both nitrogen and carbonyl oxygen, and it exists in a structure 14 in conc. sulfuric acid.

We believe that the foregoing methodology has considerable potential for the preparation of 1-azaazulenes condensed with various ring systems.

The preparation and synthetic applications of N-cycloalkenyliminophosphoranes are in progress.

ACKNOWLEDGMENT

This work was supported by an Annual Project organized by Waseda University, 1987.

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15. Orange prisms (from CH_3CN-ethyl acetate); mp 250 °C (decomp); λ_{max} (log ε) in CH_3CN: 306 (4.72), 410 (sh, 3.58), 436 (sh, 3.78), 459 (3.90), 485 (sh, 3.74).
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Received, 5th June, 1989