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REACTIONS OF PHTHALIMIDONITRENE WITH CONJUGATED ENAMINES. SYNTHESIS OF 1-AMINO-2-ETHYNYLAZIRIDINE

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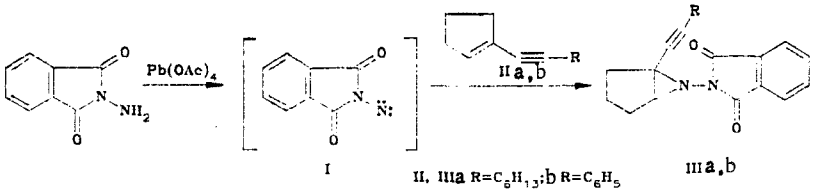
UDC 547.717'584'054.211'316.4'234.2:542.958.9

Addition of phthalimidonitrene to 1-(1-octynyl)- and 1-(phenylethynyl)-cyclopentene takes place exclusively at the double bond to give the bicyclic N-phthalimidoaziridines in ~40% yield.

Reaction of acylaminonitrenes, particularly the most thoroughly investigated phthalimidonitrene (I), with olefins provides a convenient method for the synthesis of N-aminoaziridines [1, 2]. Addition of acylaminonitrenes to conjugated dienes occurs smothly to give vinylaziridines, while acetylenes give small yields of 2-amino-2H-azirines, which are rearrangement products of the intermediate antiaromatic 1H-azirines [1, 3]. However, only one example has been reported of the reaction of the nitrene (I) with 2,5,5-trimethylhex-1-en-3-yne, a conjugated enyne system, which is present as an impurity in di-tert-butylacetylene, the reaction of which has been studied [3]. The sole addition products obtained in the latter case were the alkynylaziridines.

In order to study in greater depth the addition of acylaminonitrenes to conjugated enynes, we reacted the nitrene (I) with the alkynylcyclopentenes (II). The choice of substrates was made on the basis that the probable reaction products, namely the aziridines (III), are of considerable interest as synthons for the construction of prostanoid systems. In particular, their oxygen analogs (the corresponding epoxides) are not only used extensively in prostanoid synthesis, but have also been selected by computer as synthons for prostaglandins [4].

The reaction was carried out in the usual way [5], the nitrene (I) being generated by oxidation of N-aminophthalimide with lead tetraacetate in methylene chloride at 2-5°C in the presence of excess substrate (II). The products were isolated by column chromatography.



I II, IIIa R=C_6H_{13}; b R=C_6H_5 IIIa,b

The bicyclic aziridines (III) were obtained in yields of around 40% as yellow, crystalline solids, readily soluble in chloroform. The PMR spectra of the adducts (III) showed a signal

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for the aziridine proton at δ 4.0-4.2 ppm, replacing the poorly resolved multiplet for the olefin proton of the starting enyne (δ 5.9-6.1 ppm). The small chemical shift of the $C_{(3)}$ atom in the ^{13}C NMR spectrum of (IIIb) (δ 20.5 ppm) indicates that the 6-azabicyclo[3.1.0]-hexane moiety has the boat configuration [6].

No products resulting from additon of the nitrene (I) to the triple bond were found in the reaction mixture. This regional directivity of the reaction is in full accordance with the electrophilic character of the phthalimidonitrene (I), which we have previously demonstrated [5]. In fact, according to PES data [7], the energy of the HOMO in acetylenes is considerably less than in the corresponding ethylenes (which is apparently also the reason for the lower reactivity of acetylenes, especially those with electron-acceptor substituents, in their reactions with aminonitrenes), and therefore the HOMO of the enyne fragment must be localized for the most part on the carbon atoms of the double bond, which also determines the site of attack of the nitrene. Enynes react similarly with other electrophilic sextet species, especially dihalocarbenes and alkoxycarbonylcarbenes, when (with rare exceptions) addition of the carbene takes place predominantly (frequently exclusively) at the double bond [8, 9].

EXPERIMENTAL

NMR spectra were obtained on Tesla BS 567A and WM-400 spectrometers in chloroform, internal standard HMDS. Preparative separation was carried out by column chromatography, the purity of the products being checked by TLC on Silufol UV-254 plates (eluent hexane–ether, 2:1).

1-(1-Octynyl)- and 1-(Phenylethynyl)cyclopentene (IIa, b) were obtained in 85-95% yield by dehydration of the appropriate α-acetylenic alcohols by treatment with boron trifluoride etherate (0.5 mole per mole of alcohol) at 18-25°C in dry hexane. 1-(1-Octynyl)cyclopentene (IIa), bp 96-98°C (1.5 mm); n_D^{19} 1.4913. According to [10], bp 101-102°C (2 mm); n_D^{20} 1.4929. 1-(Phenylethynyl)cyclopentene (IIb), bp 135°C (9 mm). According to [11], bp 90°C (1 mm).

Aziridines (IIIa) and (IIIb). To a suspension of 0.81 g (5 mmole) of N-aminophthalimide [12] in 15 ml of dry, redistilled methylene chloride was added 8.8 g (50 mmole) of the enyne (IIa) or 2.6 g (15 mmole) of the enyne (IIb). The mixture was cooled with ice-water to 2-5°C, and 2.44 g (5.5 mmole) of dry lead tetraacetate [13] added in small portions over 15 min. The mixture was stirred for a further 30 min at the same temperature, then filtered through a small amount of alumina, the solid on the filter and washed with methylene chloride until the filtrate was colorless, the filtrate evaporated under reduced pressure (20-30 mm) at 18-25°C. The residual yellow oil was applied to a column of sorbent.

N-[1-(1-Octynyl)-6-azabicyclo[3.1.0]hex-6-yl]phthalimide (IIIa) was isolated by chromatography on basic alumina (Chemapol, 40/250 μm). The starting enyne (IIa) was eluted with hexane, and the product (IIIa) with a mixture of hexane and ether (2:1). Removal of the solvent under reduced pressure (20-30 mm), gave a yellow oil, which on treatment with hexane and chilling rapidly crystallized. Yield 0.66 g (39%), mp 62.5-63°C (hexane). PMR spectrum (100 MHz): 0.7-1.3 (11H, m, C_5H_{11}), 1.5-2.5 (8H, m, 2-...4-H, CH_2–C≡C), 4.04 (1H, d, J = 2.3 Hz, 5-H), 7.65 ppm (4H, AA'BB' system, phthalimide protons). Found: C 74.9; H 7.0; N 8.0%. $C_{21}H_{24}N_2O_2$. Calculated: C 75.0; H 7.2; N 8.3%.

N-[1-(Phenylethynyl)-6-azabicyclo[3.1.0]hex-6-yl]phthalimide (IIIb) was isolated by chromatography on silica gel (Silpearl), eluent a mixture of hexane and ether with an increasing amount of ether. Yield 0.62 g (38%), yellow solid, mp 154.5-155.5°C (from absolute ethanol). PMR spectrum (400 MHz): 1.5-1.8 (2H, m, 3-H), 1.9-2.15 (2H, m, 4-H), 2.28 (1H, d.d, J =13.7 and 8.2 Hz, 2-H), 2.57 (1H, d.d, J = 13.7 and 8.2 Hz, 2-H), 4.16 (1H, d, J = 3.0 Hz, 5-H), 7.0-7.2 (5H, m, C_6H_5), 7.64 (2H, m) and 7.76 ppm (2H, m, AA'BB'-system, phthalimide protons). ^{13}C NMR spectrum (100.6 MHz): 20.51 ($C_{(3)}$), 28.24 and 32.74 ($C_{(2)}$ and $C_{(4)}$), 50.26 ($C_{(1)}$), 55.62 ($C_{(5)}$); ethnyl fragment: 84.64 and 85.43; phenyl radical: 122.5 (C_i), 128.10 and 128.30 (C_m and C_p), 131.40 (C_o); phthaloyl group: 122.70 ($C_{(3)}$ and $C_{(6)}$), 130.54 ($C_{(1)}$ and $C_{(2)}$), 133.77 ($C_{(4)}$ and $C_{(5)}$), and 165.37 ppm (C=O). Found: C 77.2; H 4.8; N 7.8%. $C_{21}H_{16}N_2O_2$. Calculated: C 76.8; H 4.9; N 8.5%.

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SATURATED NITROGEN HETEROCYCLES.

11.* CATALYTIC SYNTHESIS OF 2-PYRROLIDYLALKANOLS

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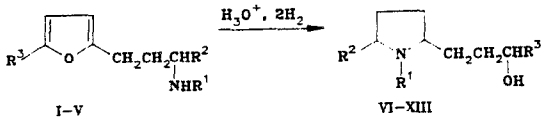
Furylakylamines have been catalytically converted into novel isomers of 2-pyrrrolidylalkanols bearing a secondary alcohol group in the aliphatic chain, or a tert-butyl group attached to the heterocycle.

Continuing studies of the conversion of furylakylamines into pyrrolidylalkanols by hydrogenation in acid media in the presence of ruthenium-promoted nickel [1], preparative methods have been developed for obtaining secondary pyrrolidylalkanols and primary alcohols containing the bulky tert-butyl radical in the 5-position of the pyrrolidine ring.



I–V VI–XIII

I, VI $R^1=R^2=H$, $R^3=CH_3$; II, VII $R^1=R^3=CH_3$, $R^2=H$; III, VIII (trans), IX (cis) $R^1=H$, $R^2=R^3=CH_3$; IV, X (trans), XI (cis) $R^1=R^2=R^3=CH_3$; V, XII (trans), XIII (cis) $R^1=R^3=H$; $R^2=t\text{-}C_4H_9$

Alcohols (VI-XIII) were obtained in acidic solution (pH 4) in the presence of skeletal nickel containing 1% of ruthenium, with an initial hydrogen pressure of 50-60 atm [2].

The presence of a methyl group in the 5-position of the furan ring reduces the rate of the reaction, so that the hydrogenation of amines (I-IV) was carried out at 70-80°C, i.e., 10-20°C higher than the other amines [1].

In the case of starting compounds (III-V), which contain an alkyl substituent in the 3-position of the side chain, both the cis- and trans-isomers are obtained, in accordance

*For Communication 10, see [1].

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