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THE REACTION OF ANTHRACENE WITH METHYLENE DIURETHANE

Cornelius K. Wilkins Jr.

Hollister Hill Laboratories, Goddard College

Plainfield, Vermont 05667

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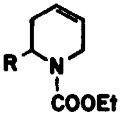
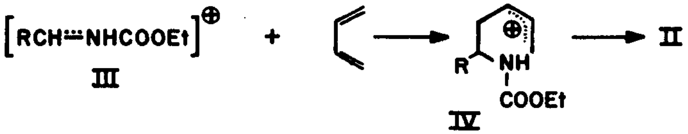
Recently the reaction of 1,1-diurethanes [i.e.(I)] with dienes in the presence of boron trifluoride etherate to yield tetrahydropyridines (II) was described (1). This reaction has provided novel synthetic routes

$RCH(NHCOOEt)_2$ I



II

to isoquinuclidene (2) and dl-anatabine (3). Little evidence has been cited concerning the mechanism of this transformation although some possibilities have been postulated (1,2). Possible mechanisms involve the attack of the diene on either a stabilized carbonium ion (III) in a clearly stepwise process(III→IV→II) or N-carbethoxyimine (V) or its BF_3 complex in a more or less concerted reaction. Examples of imines reacting as dienophiles are known (4). The isolation of telomers (VI) (la) might



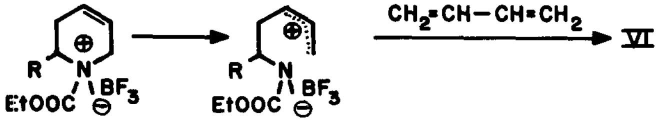
$RCH{=}NCOOEt$

V

$EtOOCNH(CH_2CH{=}CHCH_2)_nCH_2NHCOOEt$

VI

point to a stepwise reaction path although the telomers may arise via a route different from that leading to tetrahydropyridines. It is possible that the telomers are secondary products:

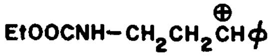


The formation of telomers (VII) from styrene (1) probably involves intermediate (VIII) in a stepwise reaction sequence.

$$\mathrm{EtOOCNH(CH\phi-CH_2)_n-RCHNHCOOEt} \qquad \mathbf{VII}$$

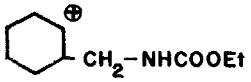
We reasoned that an intermediate of type (III) would be attacked by other pi systems such as simple olefins and activated aromatic systems. Attempted reaction of cyclohexene, mesitylene or anisole with methylene diurethane in the presence of boron trifluoride etherate at 80°, however, yielded no detectable amounts of volatile products. Phenanthrene was inert under these reaction conditions.

It is noteworthy that intermediates (IV) and (VIII) are allylic and benzylic carbonium ions respectively. In contrast, intermediate (IX) contains no stabilizing factors of this magnitude. The failure of aromatic systems to attack the reaction intermediate may reflect the low energy of intermediate (III) or (IV).



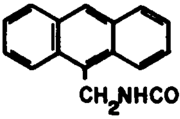
$$\mathrm{EtOOCNH-CH_2CH_2\overset{\oplus}{C}H\phi}$$

VIII

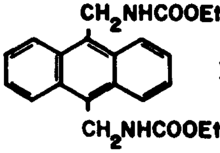


IX

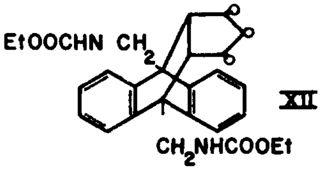
In contrast, anthracene, under the stated reaction conditions afforded 40 and 18% yields of two yellow crystalline solids m.p. 165-166.5° and 292-297° with decomposition respectively. The lower melting compound was assigned structure (X) on the basis of the following data: ν max 3300, 1680, 1257, 738 cm^{-1}, n.m.r. signals at τ8.80 (3 methyl protons, triplet, J=8.c.p.s.), 5.92 (2 methylene protons, quartet, J=8.c.p.s.), 5.12 (1 amide proton, broad), 4.73 (2 methylene protons, unsymmetrical doublet, J=5.c.p.s.), 2.80-2.28 and 2.27-1.55 (9 aromatic protons, multiplets), $\lambda_{max.}^{EtoH}$ (logϵ) 249mμ(4.96) shoulder, 254mμ(5.18), Found: C,77.66;H,6.28;N,5.14). (X) was oxidized by sodium dichromate to anthraquinone in high yield. Structure (XI) was consistent with the following data for the higher melting compound: νmax 3300, 1680, 1255, 758cm^{-1}, $\lambda_{max.}^{dioxane}$ (logϵ) 252mμ(4.85) shoulder, 258mμ(5.04), (Found: C,69.37;H,6.44;N,7.40. (XI) was also oxidized in good yield to anthraquinone by sodium dichromate. No reaction between anthracene and methylene diurethane occurred in the absence of $BF_3.Et_2O$. (X) is converted to (XI) under the reaction conditions. (XI) does not react further with methylene diurethane even at 140°. XI does, however, react with maleic anhydride at 80° to give a good yield of adduct (XII), m.p. 234-236°, νmax 3300, 1845, 1780, 1730, 1710, 1273, 759cm^{-1}, (Found: C,65.26; H,5.48;N,5.86), ϵ^{EtoH} $<10^3$.



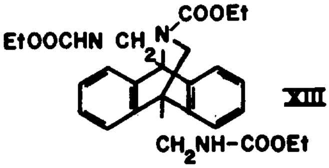
X



XI

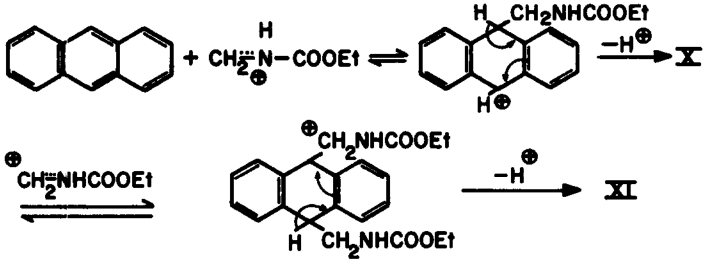


XII



XIII

Although no definite conclusion can be reached concerning the mechanism of the anthracene reaction, it seems likely that the reaction does not involve a concerted addition of an imine since (XI) fails to add a third molecule to produce (XIII), while the Diels-Adler addition of maleic anhydride is facile. It seems likely that the following reaction sequence operates:



The failure of phenanthrene to react may reflect a reactivity difference between anthracene and phenanthrene which is evident only in cases of low energy electrophiles.

The NMR spectrum was measured in deuterochloroform and the infrared spectra were taken as KBr disks.

We would like to thank Drs. M.P. Cava and I.D. Rae for their helpful suggestions.

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