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DIENE AUTOCONDENSATION OF 3,3-DIMETHYL-2-PHENYL- AND 3,3-DIMETHYL-2-(2-THIENYL)-3H-PYRROLES

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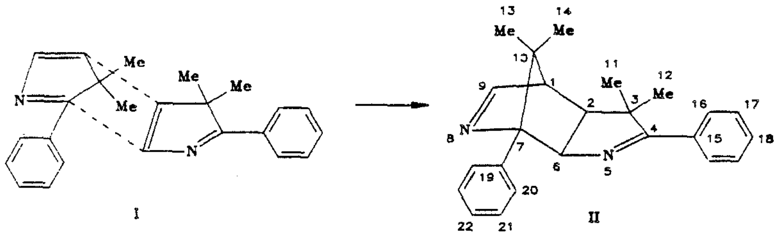
UDC 547.741.04:543.422.25

As exemplified by 3,3-diethyl-2-phenyl- and 3,3-dimethyl-2-(2-thienyl)-3H-pyrroles (obtained respectively from isopropylphenyl- and isopropyl(2-thienyl)ketoximes and acetylene [1]), we have found a new modification of the Diels–Alder condensation. This is the dimerization of 3H-pyrroles in which one molecule of 3H-pyrrole acts as an azadiene, and the other as a dienophile component:



I

II

3H-Pyrrole (I), 3.42 g, 77% pure, was kept in a glass ampul at 5-7°C for 9.5 months. The resulting crystals were washed with hexane to yield 0.6 g (23%) of 3,3,10,10-tetramethyl-4,7-diphenyl-5,8-diazatricyclo[4.3.1.$0^{2,6}$]deca-4,8-diene (II), mp 169-170°C. The mass spectrum of (II) contains the peak of the molecular ion [M^+ 342]. ^{13}C NMR spectrum (acetone-D_6): 178.41 $C_{(4)}$; 171.96 $C_{(9)}$; 139.98 $C_{(19)}$; 135.75 $C_{(15)}$; 129.92 $C_{(18)}$; 129.19; 128.65; 128.47 $C_{(16)}$; $C_{(17)}$, $C_{(20)}$; 127.42 $C_{(22)}$; 85.03 $C_{(7)}$; 81.12 $C_{(6)}$; 64.14 $C_{(3)}$; 61.70 $C_{(1)}$; 56.67 $C_{(12)}$; 50.23 $C_{(10)}$; 31.95; 22.35; 20.35; 20.07 ppm $Me_{(13)}$, $Me_{(14)}$, $Me_{(11)}$, $Me_{(12)}$. PMR spectrum (benzene-D_6): 8.27 (1H, s, 9-H); 7.3-7.8 (10H, m, Ph); 5.6 (1H, d, 6-H, $^3J_{26}$ = 7.0 Hz); 2.53 (1H, d.d, 2-H, $^3J_{12}$ = 4.0 Hz); 2.41 (1H, d, 1-H, $^3J_{12}$ = 4.0 Hz); 1.17 (3H, s, 13-Me); 1.00 (3H, s, 14-Me); 0.85 (3H, s, 11-Me); 0.56 ppm (3H, s, 12-Me). IR spectrum (KBr): 1490, 1580 (=CH, Ph), 3010, 3065 (C–H, Ph), 1600 (C=N), 1190 cm^{-1} ($\gt C(Me)_2$). The C, H, and N contents agree with the calculated values.

Of the four theoretically possible isomeric arrangements of the gem-dimethyl groups and phenyl radicals with respect to the position of nitrogen, and from the articulation of the structure, preference was given to structure (II) on the basis of multiplicity analysis and signal location in the PMR and ^{13}C NMR spectra. The signals at 178.41 and 171.96 ppm in the ^{13}C NMR spectrum are unequivocally assigned to the imine $C_{(4)}$ and $C_{(9)}$ atoms; this rejects participation of C=N bonds in the condensation.

3,3-Dimethyl-2-(2-thienyl)-3H-pyrrole is dimerized similarly in 20% yield.

The new reaction makes possible a simple approach to the hitherto unknown tricyclic systems with a partially hydrogenated pyrrolpyridine nucleus.

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0009-3122/89/2511-1314 $12.50

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DIRECT SULFONATION OF 1,3,3-TRIMETHYL-2-METHYLENEINDOLINE

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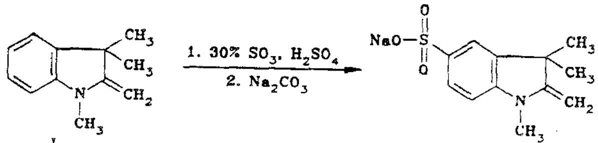
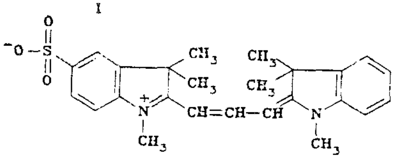
Except for 2-oxo derivatives, compounds of the indole series have not been sulfonated in the benzene ring because of their tendency to undergo oxidation [1].

We have found that when 1,3,3-trimehyl-2-methyleneindoline (I) is sulfonated with 30% oleum, 1,3,3-trimethyl-2-methylene-5-sulfoindoline (II) is formed practically quantitatively. It is of interest that, like other electrophilic substitutions, sulfonation of compound (I) in sulfuric acid medium [2] gives a 5-substituted, not a 6-substituted 2-methyleneindoline. This is shown for certain by the PMR spectrum of sulfoindoline (II) (in DMSO-D_6): 1.28 (6H, s, 3-CH_3); 3.01 (3H, s, N-$CH_3$0: 3.90 (2H, s, =CH_2); 6.58 (1H, d, J = 7.8 Hz, 7-H); 7.35 (1H, s, 4-H); 7.38 (1H, d, J = 7.8 Hz, 6-H). The PMR spectra of a large number of 5- and 6-substituted 2-methyleneindolines are shown in [2, 3]. Furthermore, to prove the structure of (II), carbocyanine (III) and styryl dye (IV) were prepared by condensation with the respective aldehydes in pyridine in the presence of trifluoroacetic acid. The synthesis of some 5-sulfoindolines (by Fischer's procedure) and of type (III) and (IV) dyes is described in a patent [4].

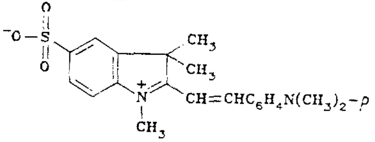


I

II



III



IV

Compound (II). Yield 97%. mp 265°C.

Compound (III). Yield 43%. mp >300°C. UV spectrum, λ_{max} (in methanol): 547 nm.

Compound (IV). Yield 72%. mp >300°C. UV spectrum, λ_{max} (in methanol): 555 nm.

S and N contents agree with the calculated values.

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