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LETTERS TO THE EDITOR

REACTION OF 2-PHENYLPYRROLE WITH 2-ACYL-1-PHENYLACETYLENES ON SILICON DIOXIDE

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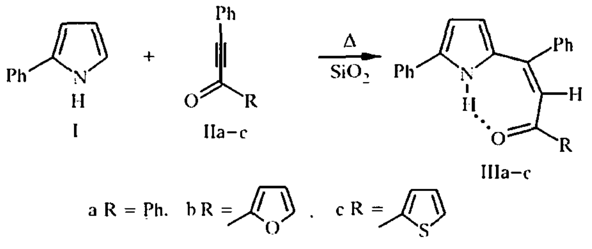
Under mild conditions (room temperature, 24 h) pyrroles react selectively with benzoylacetylene to form the C-adducts – 2-(2-benzoylethenyl)pyrroles (mixture of *E*- and *Z*-isomers) [1]. The reaction of substituted acylacetylenes with pyrroles has not been studied until now. We have shown that 2-phenylpyrrole (I) does not react with 2-benzoyl-1-phenylacetylene (IIa) under these conditions. When these reagents are heated (90°C, 10 h) 2-(2-benzoyl-1-phenylethenyl)-5-phenylpyrrole (IIIa) is formed in 40% yield, but the reaction is complicated by resin formation and the required product is difficult to isolate. The required reaction occurred much more rapidly on the surface of silica in the absence of a solvent. For example, when equimolar amounts of pyrrole I were heated with acetylene IIa or 2-furoyl- (IIb) or 2-thienoyl-1-phenylacetylene (IIc) (90°C, 1.5-2 h) in the presence of silica (Chemapol 100/250 μ silica gel, 10 fold mass excess over the weight of the reagents) the *Z*-isomers of 2-(2-acyl-1-phenylethenyl)-5-phenylpyrroles (IIIa-c) were formed exclusively in 71-89% yields.



Compounds IIIa-c are red or orange-red crystalline substances which are configurationally stable unlike the previously obtained 2-(2-benzoylethenyl-5-phenylpyrrole [1]. Formation of the *E*-isomers was not observed even on heating up to 90°C (^{1}H NMR spectroscopic data).

The ^{1}H NMR signals of the protons in the molecules of adducts IIIa-c were unambiguously assigned by homonuclear ^{1}H 2M COSY and NOESY experiments which established also that the formed *Z*-2-(2-acyl-1-phenylethenyl)5-phenylpyrroles have the *s-cis* conformation of the mutual disposition of the carbonyl fragment and the olefinic C=C bond. The unusually high signal value for the N–H proton (14.7-14.8 ppm) should also be noted. Such a weak field shift of this proton signal may be explained by intramolecular hydrogen bonding, occurrence of which is confirmed by IR spectroscopic data. So, the solid state IR spectra of compounds IIIa-c do not contain absorption bands in the 3150-3400 cm^{-1} region. Stretching vibrations of the NH group were not observed even in solutions (CCl_4) with concentrations which precluded intermolecular hydrogen bonds.

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***Z*-2-(2-Benzoyl-1-phenylethenyl)-5-phenylpyrrole (IIIa).** Mp 148-149°C (methanol). ^1H NMR spectrum ($CDCl_3$): 6.35 (1H, dd, 3-$H_{pyrrole}$); 6.67 (1H, s, CH=); 6.71 (1H, dd, 4-$H_{pyrrole}$); 7.32 (1H, m, *p*-$H_{5\text{-}Ph}$); 7.4-7.5 (8H, *m*- and *p*-H_{Ph}); 7.5-7.6 (2H, m, *o*-$H_{\alpha\text{-}Ph}$); 7.85 (2H, m, *o*-$H_{5\text{-}Ph}$); 8.03 (2H, m, *o*-H_{COPh}); 14.8 ppm (1H, br. s, NH). UV spectrum (acetonitrile), λ_{max} (log ε): 290 (4.48), 459 nm (4.37). Found, %: C 85.88; H 5.43; N 3.99. $C_{25}H_{19}NO$. Calculated, %: C 85.93; H 5.48; N 4.01.

***Z*-2-(1-Phenyl-2-furoylethenyl)-5-phenylpyrrole (IIIb).** Mp 187-187.5°C (chloroform). ^1H NMR spectrum ($CDCl_3$): 6.32 (1H, dd, 3-$H_{pyrrole}$); 6.54 (1H, dd, 4-H_{furan}); 6.58 (1H, s, CH=); 6.70 (1H, dd, 4-$H_{pyrrole}$); 7.26 (1H, dd, 3-H_{furan}); 7.30 (1H, m, *p*-$H_{5\text{-}Ph}$); 7.4-7.5 (7H, m, α-Ph and *m*-$H_{5\text{-}Ph}$); 7.60 (1H, dd, 5-H_{furan}); 7.83 (2H, m, *o*-$H_{5\text{-}Ph}$); 14.73 ppm (1H, br. s, N–H). UV spectrum (acetonitrile), λ_{max} (log ε): 296.3 (4.48), 468 nm (4.45). Found, %: C 81.01; H 5.04; N 4.09. $C_{23}H_{17}NO_2$. Calculated, %: C 81.40; H 5.05; N 4.13.

***Z*-2-(2-Thienoyl-1-phenylethenyl)-5-phenylpyrrole (IIIc).** Mp 178-178.5°C (chloroform). ^1H NMR spectrum ($CDCl_3$): 6.30 (1H, dd, 3-$H_{pyrrole}$); 6.58 (1H, s, CH=); 6.67 (1H, dd, 4-$H_{pyrrole}$); 7.11 (1H, dd, 4-$H_{thiophene}$); 7.31 (1H, m, *p*-$H_{5\text{-}Ph}$); 7.4-7.5 (7H, m, α-Ph and *m*-$H_{5\text{-}Ph}$); 7.60 (1H, dd, 5-$H_{thiophene}$); 7.75 (1H, dd, 3-$H_{thiophene}$); 7.81 (2H, m, *o*-$H_{5\text{-}Ph}$); 14.7 ppm (1H, br. s, N–H). UV spectrum (acetonitrile): λ_{max} (log ε): 267 (4.20), 301 (4.50), 469 nm (4.44). Found, %: C 77.78; H 4.77; N 3.72; S 8.85. $C_{23}H_{17}NOS$. Calculated, %: C 77.72; H 4.78; N 3.94; S 9.02.

REFERENCES

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