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EASY BROMINATION OF DIHYDROPYRIDYLIDENE- AND DIHYDROPYRIMIDINYLIDENECYANOACETIC ESTERS

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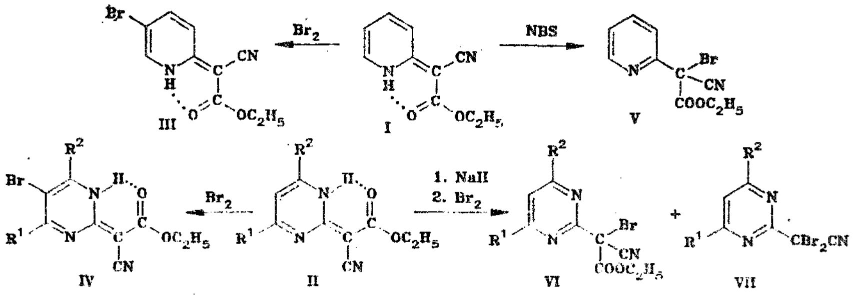
We have shown that 1,2-dihydro-2-pyridylidene- (I) and 1,2-dihydro-2-pyrimidinylidenecyanoacetic esters (IIa, b) react with bromine in acetic acid at room temperature to form the 5-bromo derivatives III and IVa, b respectively in 70-80% yield. Judging from the PMR spectra (absence of heteroaromatic proton signals in the 5.5-9.0 ppm region) at the start of the reaction (within 1-2 h) substituted hexahydropyridines and -pyrimidines form that are probably analogous to the addition products of halogens and substituted uracils in acetic acid [1, 2]. These products are detected by TLC on Silufol in chloroform (colorless material, $R_f \sim 0.6$, detection in UV light). After 30-40 h in the reaction mixture they are converted to the ylidene derivatives III and IVa, b (yellow compounds, $R_f \sim 0.3$). When the reaction is carried out at 80°, substances III and IVa, b form in 3-4 h. When bromine reacts with the sodium salts of I and II in dimethoxyethane at room temperature, bromination takes place only in the side chain, to form a mixture of mono- and dibromoderivatives V-VII (colorless compounds, $R_f \sim 0.5$). N-Bromosuccinimide (NBS) reacts with dihydropyridine I and dihydropyrimidines II in acetic acid to give monobromoderivatives of pyridine V and pyrimidines VI, respectively. In this case TLC of the reaction mixtures did not show any ring-brominated products. With the 4,6-diphenyl-substituted dihydrophyrimidine IIc bromination takes place only in the side chain (VIc, VIIc).

The elemental compositions of III-VII agree with the calculated values. The ylidene structure of the 5-bromo derivatives III, IVa, b is confirmed by IR data (intense ν_{CN} band at 2210, ν_{CO} at 1650 cm^{-1}) UV data ($\lambda_{max} > 350$ nm), and PMR data ($\delta_{NH\ldots O}$ 13-14 ppm) [3]. The products of side-chain bromination V-VII typically show no absorption bands of conjugated nitrile, but the UV spectrum has a long wave maximum at $\lambda > 300$ nm. The entrance of bromine into position 5 of dihydropyridine III and dihydropyrimidines IVa, b or into the side chain of pyridine V and pyrimidines VI and VII is evident from PMR spectral data in the region of heteroaromatic proton signals. Compound IVa was also identified by comparison with an authentic sample.



II, IV, VI, VII a $R^1=R^2=H$; b $R^1=H$, $R^2=C_6H_5$; c $R^1=R^2=C_6H_5$

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Compound shown, mp (°C), yield (%), PMR spectrum in $CDCl_3$ (δ, ppm): III, 192-194, 72, 7.20 (1H, d.d, 3-H), 7.58 (1H, d.d, 4-H), 7.71 (1H, d.d, 6-H); IVa, 191-196, 82, same as data of [3]; IVb, 198-203, 72, 7.57-7.75 (5H, m, 4-C_6H_5); 8.71 (1H, s, 6-H)[*]; V, oil, 98; 7.34 (1H, t, 5-H); 7.87 (2H, d, 3,4-H); 8.54 (1H, d, 6-H); VIa, oil, 98; 7.41 (1H, t, 5-H); 8.84 (2H, d, 4.6-H); VIb; 80-82.5, 90, 7.29-7.78; 7.89-8.26 (6H, m, 4-C_6H_5 and 5-H); VIc, 108-111, 81, 7.19-7.49, 7.89-8.16 (10H, m, 4,6-C_6H_5); 7.86 (1H, s, 5-H); VIIa, oil, 23, 7.80 (1H, t, 5-H); 8.95 (2H, d, 4,6-H)[†] VIIb, 152-155; 74; 7.36-7.66; 7.99-8.36 (6H, m, 4-C_6H_5 and 5-H); 8.99 (1H, d, 6-H)[†]; VIIc, 193-196; 80; 7.58-7.83, 8.53-8.63 (10H, m, 4,6-C_6H_5); 8.73 ppm (1H, s, 5-H)[†].

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[*] PMR spectrum of basic tautomer.

[†] PMR spectra in DMSO-D_6.