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CYCLOADDITION OF FURAN WITH NITRILIMINES

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Furan has been already demonstrated to enter as dipolarophile in 1,3-dipolar cycloadditions with nitrile oxides (1). I wish now to report the reaction of furan with another type of 1,3-dipoles, the diarylnitrilimines (I), which were prepared in situ (2) in the presence of an excess of furan.

10 mMoles of α-bromobenzal-2,4-dibromophenylhydrazine were suspended in 30 ml of furan and 14 mmoles of triethylamine were slowly added to the stirred mixture. After additional stirring for 4 hr at 20°, the reaction mixture was diluted with dry benzene and the triethylamine hydrobromide (10 mmoles) filtered off. The filtrate was evaporated under vacuum and the residue eluted through a column of silicagel (eluent benzene : cyclohexane = 70:30), giving g 1.42 (34%) of IIa, whitish crystals from ethanol, m.p. 132-133° (Found: C, 48.79; H, 2.97; Br, 38.22; N, 6.70. For $C_{17}H_{12}Br_2N_2O$ calcd.: C, 48.59; H, 2.87; Br, 38.04; N, 6.66%). UV-Spectrum: λ_{max} (C_6H_{12}) 260, 335.5 mμ; log ε 3.94, 4.20. Working at 30° gave lower yields.

Similar 1:1 adducts were prepared starting from other nitrilimines. From p.α-dichlorobenzalphenylhydrazine, triethylamine and excess furan a 21% yield of IIb, yellow platelets from ethanol, m.p. 156-157°, was obtained after 3 days at refluxing temp. (Found: C, 68.71; H, 4.42; Cl, 12.05; N, 9.33. For $C_{17}H_{13}ClN_2O$ calcd.: C, 68.80; H, 4.41; Cl, 11.94; N, 9.44%). UV-Spectrum: λ_{max} (C_6H_{12}) 248.5, 374 mμ; log ε 4.27, 4.10.

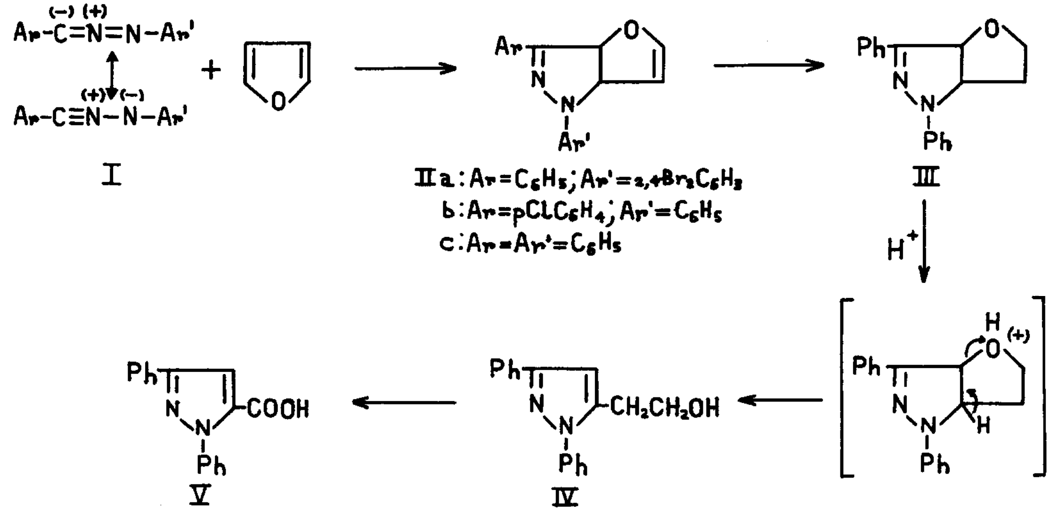
Starting from a mixture of α.chlorobenzalphenylhydrazine, triethylamine and excess furan, refluxed for 3 days, only a 6% yield of IIc pale yellow platelets from ethanol, m.p. 175-176°, was obtained (Found: C, 77.74; H, 5.38; N, 10.77. For $C_{17}H_{14}N_2O$ calcd.: C, 77.84; H, 5.38; N, 10.68%). UV-Spectrum: λ_{max} (C_6H_{12}) 245, 366 mμ; log ε 4.25, 4.30.

Structures IIa-c of 1,3-diaryl-3a,6a-dihydrofuro[3,2-c] pyrazoles were assigned on the basis of following evidence:

(i) The ultraviolet data and the blue-greenish fluorescence of the adducts are consistent for condensed Δ^2-pyrazolines.

(ii) Infrared spectra (in nujol) do not show absorption bands in the region 3500-3200 cm^{-1}.

(iii) Catalytic hydrogenation of IIa, IIb and IIc over 5% palladized charcoal gave very



I

IIa: Ar = C_6H_5; Ar' = 2,4-$Br_2C_6H_3$
b: Ar = pClC_6H_4; Ar' = C_6H_5
c: Ar = Ar' = C_6H_5

III

IV

V

good yields of the same product III, intensely fluorescent pale yellow platelets, m.p. 93-94° (Found: C, 76.84; H, 6.11; N, 10.42. For $C_{17}H_{16}N_2O$ calcd.: C, 77.25; H, 6.10; N, 10.60%).

The ultraviolet spectrum (λ_{max} (C_6H_{12}) 245, 363 mμ; log ε 4.19, 4.35) is still consistent with a Δ^2-pyrazoline structure; n.m.r. data ($CDCl_3$, TMS) also support structure III: besides the aromatic signals at δ 7.0-8.0 (8H) and multiplets at δ 2.1-2.5 (2H), δ 3.2-3.7 (1H), δ 3.8-4.2 (1H) and 4.5-4.9 (1H), a sharp doublet at δ 5.80 ppm (1H) with J 8.0 cps appears.

Refluxing III for 3 hr with 1:1 H_2SO_4 cleaved the furan ring: dilution with water gave nearly quantitative yields of a low-melting carbinol IV (IR (nujol): 3340 (broad), 1135 cm^{-1}; UV (EtOH): 264 mμ). This latter compound, not further purified, was directly oxidized with potassium permanganate in 50% aq pyridine, obtaining a 55% yield of a product, m.p. 227-230° dec., identical (mixed m.p. and infrared) with an authentic sample of 1,3-diphenylpyrazol-5-carboxylic acid (V) (3). The methyl esters were also identical.

The aforementioned results demonstrate that the double bond of the furan ring can act as dipolarophile toward the nitrilimines, whose electrophilic carbon atom attacks the α-position of the heteroaromatic ring, thus controlling the orientation of the cycloaddition.

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REFERENCES

(1) A. Corsico Coda, P. Grünanger e C. Veronesi, Tetrahedron Letters, 2911 (1966).
(2) R. Huisgen, Ang. Chem., **75**, 604 (1963).
(3) R. Huisgen, M. Seidel, G. Wallbillich and H. Knupfer, Tetrahedron, **17**, 3 (1962).