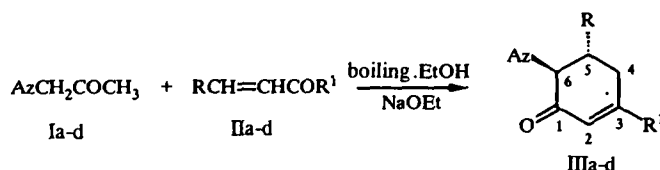


NEW REACTION OF N-ACETONYLAZOLES

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It was previously established that N-acetyl- and N-phenacylazoles reacted with α,β -unsaturated nitriles (arylmethylenemalononitriles) in the presence of base to give 5-(N-azolyl)-2-amino-4H-pyranes [1,2]. It is shown in this report that N-acetylazoles (I) give 6-membered carbocycles — cyclohexenones (III) — and not pyranes on base catalyzed reaction with α,β -unsaturated ketones (II).

15-20 mol % of base was used. The reaction was rapid (5-15 min) and stereoselective to give exclusively 50-75% of the *trans*-isomers III, as indicated by the value of $J_{H5,H6} = 13.0$ -13.5 Hz. The substituents in compounds I and II may be varied over a wide range, which makes possible the preparation of a variety of compounds III.



I, IIIa Az = benzotriazol-1-yl, b Az = 5-nitrotetrazol-2-yl, c Az = 3-nitro-1,2,4-triazol-1-yl, d Az = 4-nitroimidazol-1-yl; II and III: a R = Ph, R' = cyclopropyl, b R = 2-thienyl, R' = 2-(2-thienyl)vinyl, c R = R' = Ph, d R = Ph, R' = 2-thienyl.

^1H NMR spectra of compounds III in $(\text{CD}_3)_2\text{CO}$ and ^{13}C NMR spectra in $(\text{CD}_3)_2\text{SO}$ were recorded with a Bruker AM-300 machine with working frequencies of 300.13 and 75.47 MHz respectively.

***trans*-6-(Benzotriazol-1-yl)-5-phenyl-3-cyclopropyl-cyclohex-2-enone (IIIa).** Yield 48%. M.p. 186-187°C. ^1H NMR spectrum: 0.95-1.05 (4H, m), 1.8-1.9 (1H, m) (all $\text{H}_{\text{cyclopropyl}}$), 2.63 (1H, d.d., $J = 18.0, 4.5$ Hz, 4-H), 3.00 (1H, d.d.d., $J = 18.0, 11.7, 2.4$ Hz, 4'-H), 4.33 (1H, d.d.d., $J = 13.5, 11.7, 4.5$ Hz, 5-H), 6.14 (1H, d, $J = 2.4$ Hz, 2-H), 6.25 (1H, d, $J = 13.5$ Hz, 6-H), 7.0-7.15 (3H, m), 7.25-7.35 (3H, m), 7.41 (1H, t), 7.66 (1H, d), 7.85 ppm (1H, d) (all — H_{arom}). ^{13}C NMR spectrum: 8.2, 9.1, 18.2 (all $\text{C}_{\text{cyclopropyl}}$), 35.7 (C_4), 46.5 (C_5), 67.3 (C_6), 110.9 and 119.6 (C_{arom}), 122.0 (C_2), 123.8, 127.3, 127.5, 128.0, 128.7, 134.6, 140.7, and 145.8 (all C_{arom}), 169.6 (C_3), 191.2 ppm (C_1). Found, %: C 76.94, H 5.91, N 12.76. Calc. for $\text{C}_{21}\text{H}_{19}\text{N}_3\text{O}$, %: C 76.57, H 5.81, N 12.76.

***trans*-6-(5-Nitrotetrazol-2-yl)-5-(2-thienyl)-3-[2-(2-thienyl)vinyl]cyclohex-2-enone (IIIb).** Yield 64%. M.p. 183-186°C. ^1H NMR spectrum: 3.32 (1H, d.d.d., $J = 17.7, 12.2, 1.9$ Hz, 4'-H), 3.55 (1H, d.d., $J = 17.7, 4.7$ Hz, 4-H), 4.62 (1H, d.d.d., $J = 13.0, 12.2, 4.7$ Hz, 5-H), 6.40 (1H, d, $J = 1.9$ Hz, 2-H), 6.51 (1H, d, $J = 13.0$ Hz, 6-H), 6.90 (1H, d.d., $\text{H}_{\text{thienyl}}$), 7.02 (1H, d, $J = 16.0$ Hz, =C-H), 7.07 (1H, d), 7.13 (1H, d.d.), 7.32 (1H, d), 7.41 (1H, d), and 7.59 (1H, d) (all $\text{H}_{\text{thienyl}}$), 7.65 ppm (1H, d, $J = 16.0$ Hz, =C-H). ^{13}C NMR spectrum: 33.4 (C_4), 40.4 (C_5), 74.1 (C_6), 123.7 (C_2), 125.4, 126.1, 126.4, 127.0, 128.5, 128.9, 130.6, 131.5, 141.0 and 141.1 (all $\text{C}_{\text{thienyl}}$ and C=C), 158.5 (C_3), 165.7 (C_{Az}), and 188.6 ppm (C_1). Found, %: C 50.88, H 3.44, N 17.80, S 15.71. Calc. for $\text{C}_{17}\text{H}_{13}\text{N}_5\text{O}_3\text{S}_2$, %: C 51.12, H 3.28, N 17.53, S 16.05.

***trans*-6-(3-nitro-1,2,4-triazol-1-yl)-3,5-diphenylcyclohex-2-enone (IIIc).** Yield 75%. M.p. 167-168°C. ^1H NMR spectrum: 3.40 (1H, d.d., $J = 18.3, 5.0$ Hz, 4-H), 3.56 (1H, d.d.d., $J = 18.3, 11.1, 2.3$ Hz, 4'-H), 4.32 (1H, d.d.d., $J = 13.2, 11.1, 5.0$ Hz, 5-H), 6.07 (1H, d, $J = 13.2$ Hz, 6-H), 6.60 (1H, d, $J = 2.3$ Hz, 2-H), 7.2-7.4 (3H, m), 7.5 (5H, m),

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7.8 (2H, m) (all H_{Ph}), 8.56 ppm (1H, s, H_{Az}). ^{13}C NMR spectrum: 36.7 (C_4), 46.6 (C_5), 69.7 (C_6), 123.2 (C_2), 127.1, 128.1, 128.2, 129.4, 129.5, 131.3, 138.1, 139.8 (all C_{Ph}), 148.1 (C_{Az}), 160.8 (C_3), 163.1 (C_{Az}), 190.8 ppm (C_1). Found, %: C 67.0, H 4.08, N 15.53. Calc. for $C_{20}H_{16}N_4O_3$, %: C 66.66, H 4.48, N 15.55.

***trans*-6-(4-Nitroimidazol-1-yl)-3-(2-thienyl)-5-phenylcyclohex-2-enone (III_d)**. Yield 62%. M.p. 209-211 °C. 1H NMR spectrum: 3.47 (2H, m, 4-H and 4'-H), 4.22 (1H, d.t., $J = 13.4, 8.0$ Hz, 5-H), 5.80 (1H, d, $J = 13.4$ Hz, 6-H), 6.60 (1H, s, 2-H), 7.2-7.4 (4H, m, 3 H_{Ph} and 1 H_{Az}), 7.5-7.6 (3H, m, 2 H_{Ph} and 1 $H_{thienyl}$), 7.75 (1H, d) and 7.80 (1H, u) (both $H_{thienyl}$), 8.10 ppm (1H, d, H_{Az}). ^{13}C NMR spectrum: 36.8 (C_4), 45.8 (C_5), 66.6 (C_6), 120.1 (C_{Az}), 121.9 (C_2), 128.1, 129.3, 129.7, 130.7, and 131.8 (C_{Ph} and $C_{thienyl}$), 138.3 (C_{Az}), 139.7, 147.2 (C_{Az}), 153.0 (C_3), 192.1 ppm (C_1). Found, %: C 62.59, H 3.88, N 11.65, S 9.08. Calc. for $C_{19}H_{15}N_3O_3S$, %: C 62.45, H 4.14, N 11.51, S 8.76.

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