3-ARYL-5,5-DIMETHYL-5,6-DIHYDRO-1,2,4-TRIAZOLO[3,4-*a*]ISOQUINOLINES: A NEW EXAMPLE OF ATROPO ISOMERISM

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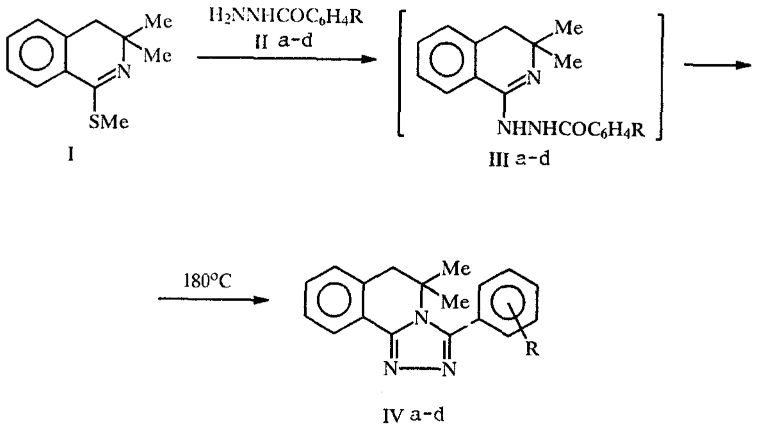
On refluxing in o-dichlorobenzene with equimolar amounts of benzoic acid hydrazides IIa-d the previously described thiolactim ether I [1] forms triazoloisoquinolines IVa-d. The reaction proceeds through a step involving the formation of [N′-(R-benzoyl)hydrazino]-3,3-dimethyl-3,4-dihydroisoquinolines IIIa-d; this was demonstrated thoroughly in the case of IIa → IIIa → IVa in the case of stepwise carrying out of the reaction in methanol (30 min, refluxing) and o-dichlorobenzene (3 h).

In the PMR spectra of IVa, b the signals of the protons of the 6-H proton and the protons of the 5-CH_3 groups are observed in the form of singlets, while for compounds with substituents R in the ortho position (IVc, d), the protons of the methyl groups give two singlet signals, whereas the CH_2 group of IVd gives a spectrum of the AB type.



II-IV a R=H, b R=4-Br, c R=2-NO_2, d R=2-Me

A study of IV by molecular mechanics (with the aid of the Alchemy II program) shows that the 3-aryl substituent cannot be located in the same plane (coplanar) as the plane of the triazoloisoquinoline system because of the presence of methyl groups attached to the $C_{(5)}$ atom, even if R = H, and free rotation about the $C_{(3)}$—$C_{(1')}$ bond is impossible. In accordance with this, the unsymmetrically [relative to the $C_{(3)}$—$C_{(1)'}$ axis] substituted IV, including IVc, d, should be produced in the form of a racemic mixture of atropo isomers. Thus, the magnetic nonequivalence of the groups of 5-CH_3 and 6-H protons in the o-R-substituted triazoloisoquinolines IVc, d is explained by their diastereotopic character.

Compound IIIa ($C_{18}H_{19}N_3O$). This compound had mp 220-222°C (methanol). IR spectrum (mineral oil): 1557, 1575, 1609, 1645, 1655, 3170 cm^{-1} (broad); 3270 cm^{-1} (broad). PMR spectrum (d_6-DMSO): 1.21 (6H, s, $2CH_3$), 2.83 (2H, s, CH_2), 6.7-8.2 (8H, m, aromatic H), 10.19 (1H, broad s, NH). The yield was 53%.

Compound IVa ($C_{18}H_{17}N_3$). This compound had mp 210-211.5°C (with sintering). IR spectrum (in mineral oil): 1595, 3060 cm^{-1}. PMR spectrum (d_6-DMSO): 1.25 (6H, s, $2CH_3$), 7.41 (3H, m, 7-9-H), 7.54 (5H, s, 2′-6′-H), 8.03 (1H, m, 10-H). The yield was 84%.

Compound IVb ($C_{18}H_{16}BrN_3$). This compound had mp 292-295°C (from the reaction mixture). PMR spectrum (d_6-DMSO): 1.25 (6H, s, $2CH_3$), 3.05 (2H, s, CH_2), 7.25-7.83 (7H, m, aromatic H), 8.03 (1H, m, 10-H). The yield was 94%.

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Compound IVc ($C_{18}H_{16}N_4O_2$). This compound had mp 194-195.5°C [2-propanol—methanol (2:1)]. PMR spectrum (d_6-DMSO): 1.22 (3H, s, CH_3), 1.30 (3H, s, CH_3), 3.13 (2H, s, CH_2), 7.49 (3H, m, 7-9-H), 7.91 (3H, m, 4′-6′-H), 8.04 (1H, m, 10-H), 8.30 (1H, dd, $J_{3',4'}$ = 8.1, $J_{3',5'}$ = 1.9 Hz, 3′-H). The yield was 94%.

Compound IVd ($C_{19}H_{19}N_3$). This compound had mp 157-158°C [heptane—2-propanol—benzene (5:2:1)]. PMR spectrum (d_6-DMSO): 1.10 (3H, s, 5-CH_3); 1.23 (3H, s, 5-CH_3; 2.13 (3H, s, 2′-CH_3); 3.02, 3.22 (2H, CH_2, J_{AB} = 16.4 Hz); 7.39 (7H, m, aromatic H); 8.04 (1H, m, 10-H). The yield was 91%.

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