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REACTIONS OF 4-NITROSO-3-THIOXO-1,2,4-TRIAZIN-5(2H)-ONES WITH β-DICARBONYL COMPOUNDS

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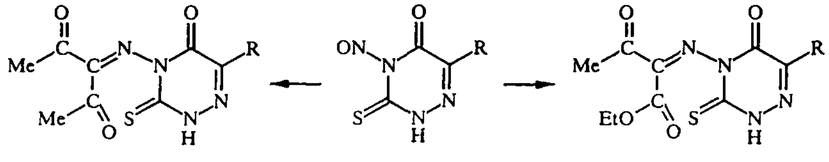
Azomethines, derivatives of 4-amino-1,2,4-triazines, have been obtained by the reaction of 4-nitroso-3-thioxo-6-R-1,2,4-triazin-5(2H)-ones with acetylacetone and ethyl acetoacetate.

The use of derivatives of 4-amino-1,2,4-triazines as selective herbicides [1] has produced an interest in the synthesis of similar compounds. However, their preparation by the reduction of known substituted 4-nitroso-1,2,4-triazines [2] is not a simple problem because loss of the nitroso groups accompanies reduction of the triazine ring. It therefore seemed worthwhile to study the possibility of other routes for the synthesis of aminotriazines. In this work, we have carried out the reaction of 4-nitrosotriazines with β-dicarbonyls (similar to the known Ehrlich–Sachs with aromatic compounds) with the aim of synthesizing azomethines — derivatives of 4-amino-1,2,4-triazines, hydrolysis of which may lead to valuable products. The azomethines are of interest themselves as potentially biologically active compounds.

We chose to study the known compounds 4-nitroso-3-thioxo-6-phenyl-1,2,4-triazin-5(2H)-one (I) and 4-nitroso-3-thioxo-6-*tert*-butyl-1,2,4-triazin-5(2H)-one (II) [3].

3-[N-(6-R-5-oxo-3-thioxo-1,2,4-triazinyl-4)]iminopentadiones-2,4 (III, IV) and ethyl 2-[N-(5-oxo-3-thioxo-6-phenyl-1,2,4-triazinyl-4)]imino-3-oxobutanoate (V) were obtained by boiling compounds I and II with acetylacetone or ethyl acetoacetate in isopropanol.



I, III, V R = Ph; II, IV R = Bu-*t*

Products III-V are crystalline solids which resinify at high temperatures and which are insoluble in water and ethanol. Their structures were determined by a combination of elemental analysis and IR, NMR, and UV spectra.

The band at 1485-1500 cm^{-1}, characteristic of the nitroso groups in the starting materials I and II, was absent from the IR spectra of azomethines III-V. The absorption bands of the carbonyl groups of the triazine ring were retained: 1645 (III), 1675 (IV), and 1645 cm^{-1} (V). The spectra also contained bands at 1685-1680 cm^{-1}, absent from the spectra of the starting materials, which may be ascribed to carbonyl stretches of the substituents at position 4 of the heterocycle.

The electronic spectra of compounds III-V differ comparatively slightly from the spectra of the initial triazines I and II. In these, there is also a group of four bands at 240.8-258.3 nm (lg ε = 2.6-2.8). The absorption band at 293.3 nm (lg ε = 4.23) is ascribed to the $\pi-\pi^*$ transition in the conjugated system $-C(S)-N=N-C(R)=C(OH)-$, while that at 362.5 nm (lg ε =4.47-4.59) is ascribed to charge transfer in the $-C(S)-NH-N=C(Ph)$-, which agrees with literature data [4, 5]. The absorption of the $Me-C(O)-C=N-$ group in the 240-250 nm region is overlapped by the more intense absorption of the triazine ring as is observed in semicarbazones [4]. There is also an absorption maximum at 202.5 nm, which is absent from the spectra of the starting materials I and II, which is evidently connected with an $n-\pi^*$ electron transition in the carbonyl

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group as evidenced by the small extinction coefficient (lg ε = 0.74-0.76). An absorption maximum at 366 nm (lg ε = 2) corresponding to the $n-\pi^*$ electron transition in the nitroso group is absent from the spectra of products III-V.

Signals of the protons of the substituents at position 6 of the ring — 1.24 (s, Bu-*t*) and 7.27-7.78 (m, Ph) — and two singlets of equal intensity at 11.55 and 12.27 (IV) and 10.23 and 10.9 ppm (III), corresponding to signals of protons of the SH $\rightleftarrows$ $N_{(2)}H$ group appear in the ^1H NMR spectra of compounds III and IV. Singlets at 2.8-3.0 ppm belong to the MeC(O) group. These signals are absent from the spectra of the starting materials I and II.

The ^{13}C NMR spectrum of compound III contains signals for the carbon atoms of the phenyl substituent at 128-130 ppm and at $C_{(3)}$ 146, $C_{(6)}$ 132, and $C_{(5)}$ 131 ppm for the atoms of the triazine ring, which is in good agreement with literature data [6]. The signals at 174.0, 153.8, and 39.5 ppm correspond to the C=O, C=N, and CH_3 groups of the substituent at position 4 of the heterocycle.

The mechanism of the process suggests the normal interaction of amines with carbonyl compounds with this difference, that addition of the anion at the π bond of the N=O group rather than the C=O group. Sodium carbonate catalyzes the enolization and subsequent loss of water from the intermediate product. With an excess of the nitroso, there is the danger of a side reaction, formation of the azomethine N-oxide (nitrone). However, the spectra of the reaction products did not indicate its presence. Absorption bands at 1250-1310 and 950-970 cm^{-1}, corresponding to stretching vibrations of the N→O group [4], were absent from the IR spectra of compounds III-V.

EXPERIMENTAL

IR spectra of KBr disks were recorded with a UR-10 instrument, ^1H [$(CD_3)_2CO$ solutions] and ^{13}C (DMSO-D_6 solutions) NMR spectra were obtained with Tesla 85-487B (80 MHz) and WM-360 (360 MHz) spectrometers respectively with HMDS as internal standard. Electronic spectra of dioxane solutions (c = 10^{-3} mol dm^{-3}) were recorded with a Beckman instrument. Purity of products was monitored by TLC on Silufol UV-254 strips with 5:1 chloroform–acetone as eluant.

The starting materials I and II were prepared by a literature method [3]. Their characteristics (m.p. 183-210 (decomp) for I and m.p. 235-250°C (decomp) for II) agreed with literature values [3].

3-[N-(5-oxo-3-thioxo-6-phenyl-1,2,4-triazinyl-4)]iminopentadione-2,4 (III). Compound I (0.01 mol) was dissolved with stirring in isopropanol (50 cm^3) containing $Na_2CO_3\cdot10H_2O$ (0.01 mol) and acetylacetone (0.01 mol) was then added. The reaction mixture was boiled for 4-4.5 h, cooled, and the precipitate was filtered off. Dilute HCl was added to the filtrate to a pH of 6-7. The precipitate of compound III was filtered off, dried in air, and recrystallized from isopropanol, yield 76%. mp 256-262°C (resinified). IR spectrum: 3435 (NH), 1685, 1645 (C=O), 1160 (C=S), 1570, 1520, 1450, 1410, 1300 (C=C, C=N), 1115, 1080, 1040, 885 cm^{-1} (heterocycle). UV spectrum, λ_{max} (lg ε): 362.5 (4.57), 293.3 (4.23), 258.3 (2.86), 246.7 (2.64), 252.5 (2.58), 240.8 (2.61), 202.5 nm (0.74). ^1H NMR spectrum: 7.27-7.78 (5 H, m, Ph), 10.23 and 10.90 (0.5 H and 0.5 H, two s, SH $\rightleftarrows$ NH), 3.00 ppm (6 H, s, 2 Me). ^{13}C NMR spectrum: 128-130.3 ($C_{(Ph)}$), 146 ($C_{(3)}$), 132.2 ($C_{(6)}$), 131.2 ($C_{(5)}$), 174.4 (C=O), 153.8 (C=N), 39.5 ppm (Me). Found, %: C 52.9, H 3.9, N 17.2. Calc. for $C_{14}H_{12}N_4O_3S$, %: C 53.1, H 3.8, N 17.7.

3-[N-(6-*tert*-butyl-5-oxo-3-thioxo-1,2,4-triazinyl-4)]iminopentadione-2,4 (IV). Compound IV was prepared from compound II by the method described above. Yield 84%. M.p. 280°C (subl.). IR spectrum: 3570 (NH), 2970, 2920 (Me), 1680, 1675 (C=O), 1200 (C=S), 1590, 1555, 1485, 1450 (C=C, C=N), 1080, 995, 930, 885 cm^{-1} (heterocycle). UV spectrum, λ_{max} (lg ε): 293.3 (4.23), 258.3 (2.86), 252.5 (2.58), 246.7 (2.64), 240.8 (2.61), 202.5 nm (0.74). ^1H NMR spectrum: 1.24 (9 H, s, Bu-*t*), 2.8 (6 H, s, MeC=O), 11.55 and 12.27 ppm (0.5 H and 0.5 H, two s, HS $\rightleftarrows$ NH). Found, %: C 48.4, H 5.3, N 19.1. Calc. for $C_{12}H_{16}N_4O_3S$, %: C 48.6, H 5.5, N 18.9.

Ethyl 2-[N-(5-oxo-3-thioxo-6-phenyl-1,2,4-triazinyl-4)]imino-3-oxobutanoate (V). Product V was prepared analogously to compounds III and IV from compound I and ethyl acetoacetate. Yield 64%. M.p. 252-255°C (resinification). IR spectrum: 3450 (NH), 1690, 1680, 1645 (C=O), 1165 (C=S), 1570, 1530, 1450, 1420, 1330 (C=C, C=N); 1040, 1030, 1000, 990 cm^{-1} (heterocycle). UV spectrum, λ_{max} (lg ε): 362.5 (4.59), 293.3 (4.26), 258.3 (2.89), 252.5 (2.61), 246.7 (2.66), 240.8 (2.63), 202.5 nm (0.76). Found: %: C 52.6, H 2.6, N 16.5. Calc. for $C_{15}H_{14}N_4O_4S$, %: C 52.8, H 2.7, N 16.4.

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