LETTERS TO THE EDITOR

ACETYLATION OF 2,3,6-TRIPHENYL- AND 1-METHYL-2,3,6-TRIPHENYL-4-PIPERIDONE

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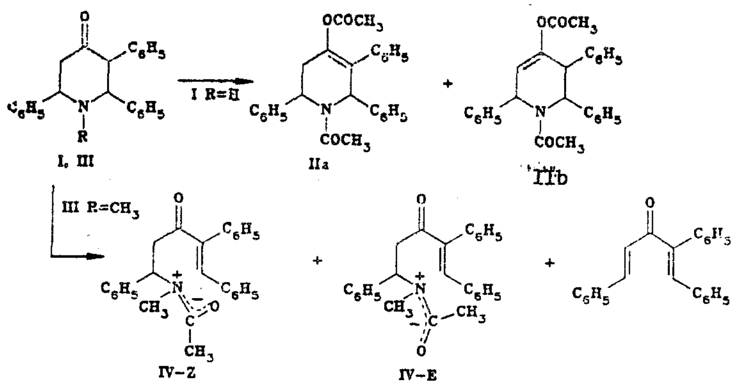
No information regarding 4-piperidone enol esters is available in the literature. We have established that 1-acetyl-4-acetoxy-2,3,6-triphenyl-1,2,5,6-tetrahydropyridine (IIa, mp 139-140°C) and the isomeric 1,2,3,6-tetrahydropyridine IIb (mp 135°C) are formed when a mixture of 2,3,6-triphenyl-4-piperidone (I) and acetic anhydride (in a ratio of 1:8) is heated briefly to the boiling point and then maintained at 20°C for several hours in the presence of pyridine. Enol esters IIa and IIb were isolated chromatographically in 38% and 16% yields, respectively. Their mass spectra contain maximally intense molecular-ion peaks M$^+$ 411. In the IR spectra the absorption bands at 1753 cm^{-1} are related to an ester group, while the bands at 1655 cm^{-1} are related to an amido group. PMR spectrum (CDCl$_3$) of IIa: 2.10 (s, 3H), 2.13 (s, 3H), 3.0 and 2.83 (dd, J = 16.4, 8.2, and 7.0 Hz, 2H, 5a- and 5e-H), 5.28 (t, 1H, J = 8.2 and 7.0 Hz), 6.8-7.6 ppm (m, 16H, 2-H and aromatic protons). PMR spectrum of IIb: 1.67 (s, 3H), 2.14 (s, 3H), 4.48 (broad s, 1H, 3-H), 5.32 (broad s, 1H, 2-H), 6.09 (d, 1H, J = 4.3 Hz, 5-H), 6.60 (d, 1H, J = 4.3 Hz, 6-H), 6.8-7.5 ppm (m, 15H, aromatic protons).



An enol ester is not formed from 1-methyl-2,3,6-triphenyl-4-piperidone (III) under similar conditions. In this case a mixture of Z and E isomers with respect to the amido group of 5-(N-acetyl-N-methylamino)-1,2,5-triphenyl-1-penten-3-one (IV) (in a ratio of 1:1) was obtained in 36% yield as a result of ring cleavage; the mixture had mp 142-144°C. IR spectrum, ν, cm^{-1}: 1677 and 3480 (broad bands), 1583, 1595, 1630, 1650 sh, 1690 sh, 1710 sh. In the PMR spectrum of amide IV (CDCl$_3$) the two CH$_3$ groups show up in the form of four singlets with an integral intensity of 1.5H each at 2.08 and 2.61 ppm (Z isomer) and 2.34 and 2.71 ppm (E isomer). The signal of the 5-H proton also has a different chemical shift for each isomer [the triplets at 5.69 and 6.25 ppm with an integral intensity of 0.5H each and a spin-spin coupling constant (SSCC) of 7.0 Hz correspond to the Z and E isomers]. The remaining protons of amide IV resonate at 7.69 (s, 1H, 1-H), 6.90-7.60 (m, 15H), and 2.86-3.55 ppm (m, 2H, 4-CH$_2$). Similar opening of the 2,2,6,6-tetramethylpiperidine ring was described in [1]. In addition to amide IV, 1,2,5-triphenyl-1,4-pentadien-3-one (V) (24% yield, mp 112°C [2]) was isolated chromatographically from the reaction products. Dienone V was obtained in 70% yield also by heating amide IV in acetic anhydride.

In the case of piperidone I the first step is N-acetylation, which promotes its enolization. This is evidently followed by an N$\rightarrow$O acyl rearrangement [3], which fixes the enol in the ester form, after which N-acylation again occurs.

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The results of elementary analysis were in agreement with the calculated values.

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UNUSUAL REACTION OF A CYCLIC THIOCARBONATE WITH SECONDARY AMINES

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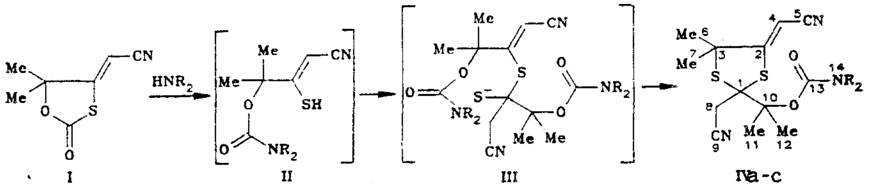
We have established that 2-[1-(N,N-dialkylcarbamoyloxv)-1-methylethyl]-5,5-dimethyl-2-cyanomethyl-4-cyanomethylene-1,3-dithiolanes IV are formed in uo to 90% yields instead of the expected (in accordance with [2, 3]) carbamates II in the reaction of 1,3-oxathiolan-2-one I [1] with secondary amines.



I II III IVa-c

IV a R=Et; b R=Pr; c R=Bu

Opening of the 1,3-oxathiolane ring with the formation of β-mercaptoalkylcarbamate II evidently occurs in the first step under the influence of the amine; the subsequent dimerization of II via the addition of the mercapto group of one molecule to the double bond of a second molecule leads to intermediate III. This is followed by intramolecular substitution of the carbamoyl grouping with the formation of the 1,3-dithiolane ring.

The structures of dithiolanes IVa-c were established by x-ray diffraction analysis and were confirmed by ^{1}H and ^{13}C NMR spectroscopy and the IR spectra.

2-[1-(N,N-Diethylcarbamoyloxy)-1-methylethyl]-5,5-dimethyl-2-cyanomethyl-4-cyanomethylene-2,3-dithiolane (IVa, $C_{17}H_{25}N_3O_2S_2$). This compound was obtained in 92% yield and had mp 158-160°C (from ether). IR spectrum ($CHCl_3$): 1570 (SC=CH), 1680 (C=O), 2215 (C=CHCN), 2245 cm^{-1} (CH_2CN). ^{1}H NMR spectrum ($CDCl_3$), δ: 5.26 (1H, s, =CH), 3.42 (4H, q, CH_2N), 3.17 (2H, s, CH_2), 1.84 (6H, s, CH_3),. 1.71 (6H, s, CH_3), 1.13 ppm (6H, t, CH_3). ^{13}C NMR spectrum ($CDCl_3$): 86.1 [$C_{(1)}$], 153.5 [$C_{(2)}$], 64.8 [$C_{(3)}$], 88.9 [$C_{(4)}$], 116.2 and 118.1 [$C_{(5)}$, $C_{(9)}$], 31.9 [$C_{(8)}$], 72.4 [$C_{(10)}$], 173.2 [$C_{(13)}$], 41.7 [$C_{(14)}$], 28.8, 31.6, 13.5 [$C_{(6)}$, $C_{(7)}$, $C_{(11)}$, $C_{(12)}$, $C_{(14)}$].

2-[1-(N,N-Dipropylcarbamoyloxy)-1-methylethyl[-5,5-dimethyl-2-cyanomethyl-4-cyanomethylene-1,3-dithiolane (IVb, $C_{19}H_{27}N_3O_2S_2$). This compound was obtained in 91% yield in the form of a light-yellow oil. IR spectrum (microlayer): 1560 (SC=CH), 1700 (C=O), 2220 (C=CHCN), 2250 cm^{-1} (CH_2CN). ^{1}H NMR spectrum ($CDCl_3$), δ: 5.27 (1H, s, =CH), 3.34 (10H, m, CH_2), 1.84 (6H, s, CH_3), 1.75 (6H, m, CH_3), 1.55 ppm (6H, m, CH_3).

2-[1-(N,N-Dibutylcarbamoyloxy)-1-methylethyl]-5,5-dimethyl-2-cyanomethyl-4-cyanomethylene-1,3-dithiolane (IVc, $C_{21}H_{33}N_3O_2S_2$). This compound was obtained in 92% yield in the form of a light-yellow oil. IR spectrum (microlayer): 1560 (SC=CH), 1700 (C=O), 2200 (C=CHCN), 2250 cm^{-1} (CH_2CN). ^{1}H NMR spectrum ($CDCl_3$), δ: 5.27 (1H, s, =CH), 3.29 (4H, q, CH_2), 3.21 (10H, m, CH_2), 1.77 (6H, s, CH_3), 1.71 (6H, d, CH_3), 0.94 ppm (6H, m, $2CH_3$).

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