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RING-CHAIN ISOMERIZATION IN A SERIES OF β-HYDROXY-OXOENAMINES. SYNTHESIS OF 2-AMINO-5,5-DIALKYL-2-TRICHLOROMETHYL-4-TETRAHYDROPYRONES AND 5,5-DIALKYL-2-TRICHLOROMETHYL-4-DIHYDROPYRONES

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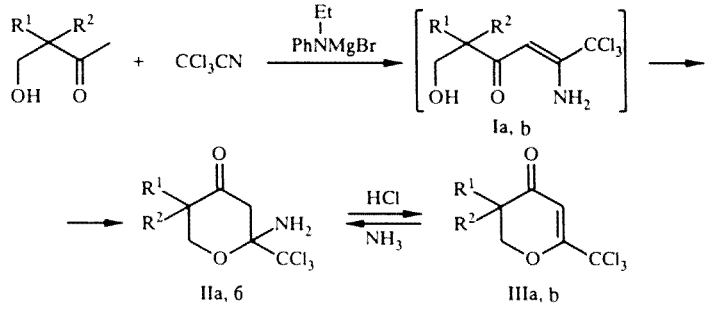
One of us showed earlier [1] that the reaction of trichloroacetonitrile with diacetone alcohol as methylene source in the presence of N-ethyl-N-phenylaminomagnesium bromide gave 2-amino-6-hydroxy-6-methyl-1,1,1-trichloromethyl-2-hepten-4-one which was stable to storage and existed only in the acyclic form.

We have found when diacetone alcohol is replaced by its isomer with *gem*-dimethyl groups at the carbonyl atom — 4-hydroxy-3,3-dimethyl-2-butanone — the reaction with trichloroacetonitrile does not stop at the open chain hydroxyoxoenamine state (Ia) but is accompanied by spontaneous cyclization to 2-amino-5,5-dimethyl-2-trichloromethyl-4-tetrahydropyrone (IIa). The condensation of trichloroacetonitrile with 1-acetyl-1-hydroxymethylcyclohexanone occurs analogously to give the spirotetrahydropyrone (IIb). Compounds IIa and IIb were isolated by decomposition of their copper chelates with hydrogen sulfide, but the β-hydroxyoxoenamines were not observed even as impurities.

The tetrahydropyrones IIa and IIb were converted almost quantitatively by treatment with concentrated HCl at room temperature into the dihydropyrones IIIa and IIIb and the latter readily added ammonia in methanol solution to give compounds IIa and IIb.

The spontaneous cyclization of β-hydroxyoxoenamines Ia and Ib into the tetrahydropyrones IIa and IIb is the first example of ring-chain isomerism among aliphatic enamines containing β-ketone groups. It is evidently related to the steric effect of the *gem*-dimethyl group at the carbonyl carbon on the configurational mobility of the molecule. The cyclization of the imines of 5-hydroxypentanal into 2-alkylaminotetrahydropyranes may be a close analog [2].



I–III a $R^1 = R^2 = Me$, b $R^1 + R^2 = (CH_2)_5$

2-Amino-5,5-dimethyl-2-trichloromethyl-4-tetrahydropyrone (IIa). Yield 15%. mp 116-117°C (ethanol). IR spectrum (Nujol): 3410, 3330 (NH_2), 1710 (C=O), 1620 cm^{-1} (NH_2). ^1H NMR spectrum ($CDCl_3$): 1.02 (3H, s, CH_3), 1.32 (3H, s, CH_3), 2.07 (2H, s, NH_2), 2.54, 3.32 (2H, dd, J = 14.8 Hz, 3-CH_2), 3.68, 4.14 ppm (2H, dd, J = 11.0 Hz, 6-CH_2). Found, %: C 37.06, 37.03; H 4.60, 4.62; N 5.25, 5.24. Calc. for $C_8H_{12}Cl_3NO_2$, %: C 36.88, H 4.64, N 5.38.

2-Amino-5,5-pentamethylene-2-trichloromethyl-4-tetrahydropyrone (IIb). Yield 45%. mp 130-131°C (ethanol). IR spectrum (Nujol): 3420, 3330, 3120 (NH_2), 1710 (C=O), 1620 cm^{-1} (NH_2). ^1H NMR Spectrum ($CDCl_3$): 1.1-1.9 (10H,

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m, cyclohexane ring), 2.04 (2H, s, NH_2), 2.50, 3.32 (2H, dd, J = 14.5 Hz, 3-CH_2), 3.95, 4.03 ppm (2H, dd, J = 11.4 Hz, 6-CH_2). Found, %: C 44.02, 44.06; H 5.56, 5.40; N 4.60, 4.44. Calc. for $C_{11}H_{16}Cl_3NO_2$, %: C 43.95, H 5.37, N 4.66.

5,5-Dimethyl-2-trichloromethyl-4-dihydropyrone (IIIa). Yield 92%. mp 85-86°C (pentane). IR spectrum (Nujol): 1690 (C=O), 1615 cm^{-1} (C=C). ^1H NMR spectrum ($CDCl_3$): 1.16 (6H, s, $2CH_3$), 4.30 (2H, s, CH_2), 6.10 ppm (1H, s, =CH). Found, %: C 39.56, 39.26, H 3.69; 3.78. Calc. for $C_8H_9Cl_3O_2$, %: C 39.46, H 3.73.

5,5-Pentamethylene-2-trichloromethyl-4-dihydropyrone (IIIb). mp 67-68°C (hexane). IR spectrum (Nujol): 1690 (C=O), 1620 cm^{-1} (C=C). ^1H NMR spectrum ($CDCl_3$): 1.2-1.9 (10H, m, cyclohexane ring), 4.44 (2H, s, CH_2), 6.05 ppm (1H, s, =CH). Found, %: C 46.66, 46.56; H 4.61, 4.77. Calc. for $C_{11}H_{13}Cl_3O_2$, %: C 46.59, H 4.62.

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