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AN OLIGO VICINAL DIIMINE BY THE EHRLICH-SACHS REACTION OF A β-IMINOKETONE WITH NITROSOBENZENE

Submitted by (01/03/95)

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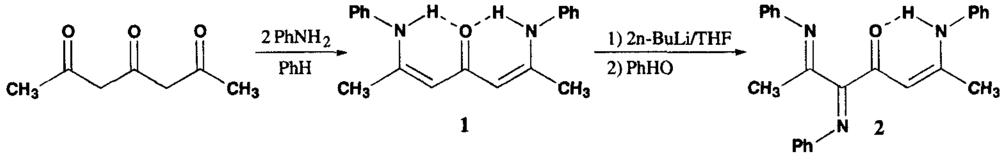
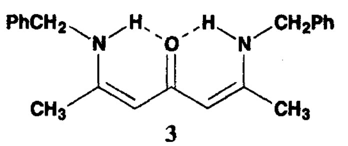
Interest in the spectra of helical polyisocyanides and, especially of a simpler homologous series of oligo vicinal imines has led to the study of preparation of acyclic *vic*-triimines and higher homologs.[1] The condensation of C-nitroso compounds with active methylene compounds in the presence of a base, produces either imines (Ehrlich-Sachs)[2] and/or nitrones(Krohnke)[3] depending on reactants and conditions. Although no clear explanation defines the anil/nitrone product ratio, high temperature, strong base, absence of water, weak intramolecular hydrogen bonding between the two β-dicarbonyl groups, and short reaction time favor imine formation. On the other hand, low temperature, weak base, presence of water, strong intramolecular hydrogen bonding between the two β-dicarbonyl groups, excess nitrosobenzene, and long reaction time appear to promote nitrone formation.[4-7] The Ehrlich-Sachs reaction has never been utilized for the formation of *vic*-triimines and pentaimines.Although it has already been applied to various β-dicarbonyl amides and esters and their monoanil derivatives[8-12], the formation of *vic*-imines from β-iminoketones has never been reported in the literature. The successful extension of Ehrlich-Sachs reaction to β-iminoketones is not a straight forward process. Differences in the acidity of the most active methylene group, in the degree of enolization and in the stability of H-bonded *quasi*-six membered rings, such as shown in structures **1** and **2** may affect the resulting anil/nitrone ratio.[11] We now report the successful extension of the Ehrlich-Sachs reaction to 2,6-dianilinohept-2,5-dien-4-one **1**, a β-iminoketone, which was obtained by the azeotropic distillation of water from the reaction of aniline with 2,4,6-heptanetrione.



Compound **1** exists predominantly as the ketodienamine. Its IR spectrum shows an absorption band at 1660 cm^{-1} for conjugated C=O and no absorption at 3200-3500 cm^{-1}, expected for -OH or -NH groups. The PMR spectrum displayed a singlet for two equivalent -CH_3 groups at δ 1.95, another singlet for two vinylic hydrogens at δ 4.85, a multiplet for the ten aromatic hydrogens at δ 6.85-7.45, and a broad singlet for N-H at δ 12.3-12.5.The ketodienamine structure was more easily demonstrated from the PMR spectrum of the related 2,6-di(benzylamino)hept-2,5-dien-4-one (**3**) (prepared analogously to **1**), which exhibited the following signals: a singlet for two equivalent -CH_3 groups at δ 1.85, a doublet for the N-methylene groups at δ 4.35, a singlet for two vinylic hydrogens at δ 4.75, a singlet for the ten aromatic hydrogens at δ 7.25, and a broad singlet at δ 10.5-10.8. No other signals either for the N-methylenes or the C-methylenes were detected.



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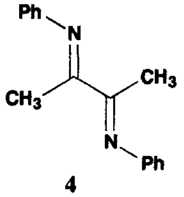

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The condensation of **1** with nitrosobenzene in the presence of two equivalents of *n*-BuLi in THF under N_2 produced **2**, which also exists predominantely as a ketoenamine. Its IR spectrum shows absorptions at 1685 cm^{-1} and 3335 cm^{-1} for conjugated C=O and N-H, respectively, while its PMR spectrum displayed two singlets for two $-CH_3$ groups at δ 1.85 and 2.15, another singlet at δ 5.50 for one vinylic hydrogen, and a broad multiplet at δ 6.35-7.50 for 15 aromatic hydrogens. While compound **2** showed a UV absorption band at 323 nm ($\varepsilon_{CH_2Cl_2}$ = 7,938), the conformation of the two imine units in N,N'-(1,2-dimethyl-1,2-ethanediylidene)*bis*(benzeneamine) [**4**] was reported to be coplanar, *s-trans*, with a UV absorption at 335 nm ($\varepsilon_{95\%\ EtOH}$ = 2,875).[9,13] Thus, one might assume that the two anil groups and the keto group in **2** are in three different perpendicular planes as shown by its UV absorption at 323 nm which appears at the same wavelength as 4-anilino-3-penten-2-one.[14] All attempts to condense nitrosobenzene, including the use of higher temperature and longer reaction time, with **2** or **3** led only to the recovery of the starting material. These unsuccessful attempts show that the Ehrlich-Sachs reaction is not always a general route for the preparation of *vic*-oligodiimines from β-iminoketones.

EXPERIMENTAL SECTION

All mps. were determined on a Fisher-Johns melting point apparatus and are uncorrected. Infrared spectra were recorded asKBr pellets on a Perkin-Elmer model 710B spectrometer. Proton magnetic resonance spectra were determined in $CDCl_3$ with a Hitachi Perkin-Elmer (60 MHz) R-24-B instrument using TMS as an internal standard.All UV spectra were taken in a 10mm pathlength quartz cell and were recorded with a Cary 14 ultraviolet spectrophotometer. Microanalyses were performed by Spang Microanalytical Laboratories, Eagle Harbor, Michigan. 2,4,6-Heptanetrione was prepared in accordance with the literature.[15]

2,6-Dianilinohept-2,5-dien-4-one (1).- 2,4,6-Heptanetrione (0.71 g, 0.005 mol) and aniline (3.73 g, 0.04 mol) were azeotropically refluxed for 4 hrs in 30 mL of benzene. The resulting reaction mixture was washed with 2 x 15 mL 10% HCl, 10 mL H_2O, and then dried over anhydrous $MgSO_4$. The organic layer was filtered and the solvent was evaporated using a rotary evaporator. On cooling, a yellow green solid was formed, which upon recrystallization from ethanol yielded 0.84 g (58%) of a yellow solid, mp. 131.5-133°.

Anal. Calcd. for $C_{19}H_{20}N_2O$: C, 78.05; H, 6.90; N, 9.58. Found:C, 77.97; H, 7.03; N, 9.47

2-Anilino-5,6-phenylimino-2-hepten-4-one (2).- *n*-Butyllithium (1.6 M in hexane) (3.1 mL, 0.005 mol) was added slowly to a stirred solution of 2,6-dianilinohept-2,5-dien-4-one **1** (0.73 g, 0.0025 mol) in 20 mL of THF. The reaction mixture was stirred under N_2 for 5 minutes at room temperature. To the resulting reddish brown solution, nitrosobenzene (0.27 g, 0.0025 mol) was added. After 4.5 hrs of stirring under N_2 at room temperature, 5 mL of water was added and the solvent was evaporated using a rotary evaporator.The resulting yellowish brown solid was washed with 10 mL of ethanol to yield 0.88g (92%) of a white solid, mp. 162° (dec.).

Anal. Calcd. for $C_{25}H_{23}N_3O$: C, 78.71; H, 6.08; N, 11.02. Found: C, 78.57; H, 6.17; N, 10.81

2,6-Dibenzylaminohept-2,5-dien-4-one (3).- 2,4,6-Heptanetrione (5.28 g, 0.037 mol) and benzylamine (12.00 g, 0.112 mol) were azeotropically refluxed for 6.5 hrs in 30 mL of benzene. On cooling, an orange yellow solid was formed, which upon recrystalization from absolute ethanol yielded 7.80 g (66%) of a yellow solid, mp. 120-121°.

Anal. Calcd. for $C_{21}H_{24}N_2O$: C, 78.71; H, 7.55; N, 8.74. Found: C, 78.64; H, 7.59; N, 8.82

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