Found: C 59.5; H 5.4; N 10.7%; M 262 by mass spectrometry. C_{25}H_{24}N_{10}O_{4}. Calculated: C 59.5; H 5.4; N 10.7%; M 262.26.

LITERATURE CITED


SYNTHESIS AND STEREOCHEMISTRY OF N-SUBSTITUTED 3,5-DIBENZOYL-4-PHENYLPIPERIDINES

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The addition of methyl-, benzyl-, cyclohexyl, and 2-hydroxyethylamines and hydroxylamine to 2,4-dibenzoyl-3-phenyl-1,4-pentadiene in dimethylformamide leads to the formation of stereoisomers of the corresponding N-substituted 3,5-dibenzoyl-4-phenylpiperidines in almost quantitative yields. The configurations of the stereoisomers obtained were determined by PMR spectroscopy, and their interconversions under the influence of alkali were studied.

In a preliminary communication [2] we described the formation of the α and β forms of N-substituted 3,5-dibenzoyl-4-phenylpiperidines (II, III) by the reaction of, respectively, methyl- and benzylamine with 2,4-dibenzoyl-3-phenyl-1,4-pentadiene (I). In the present paper we present data on the addition of primary amines and hydroxylamine to diketone I and on the stereochemistry and interconversions of the resulting stereoisomeric piperidines II–VI.

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The reaction takes place in dimethylformamide (DMFA) at room temperature and gives the products in almost quantitative yields.

The structures of II-VI (Table 1) follow from a comparison of their IR spectra with the spectrum of diketone I [3], which has absorption bands at 1660 (C=O) and 1630 cm\(^{-1}\) (C=CH\(_2\)). The IR spectra of piperidines II-VI do not contain the absorption of a C=CH\(_2\) group, but a C=O band is found at 1680-1690 cm\(^{-1}\).

Each II-V consists of a mixture of two \(\alpha\) and \(\beta\) stereoisomers, while VI consists of a mixture of three isomers \(-\alpha, \beta,\) and \(\gamma\). The isomer ratios II\(\alpha\):II\(\beta\) = 3:1 and VI\(\alpha\):VI\(\beta\):VI\(\gamma\) = 11:8:1 were found by means of column chromatography on silica gel. The \(\alpha\) isomers in the remaining cases are obtained in high yields. They have large \(R_f\) values, similar PMR spectra (Table 2), and, except for III\(\alpha\), are characterized by higher melting points and lower solubilities than the corresponding \(\beta\) isomers.

The action of catalytic amounts of NaOH on alcohol solutions of II\(\beta\)-VI\(\beta\) leads to their isomerization to the corresponding II\(\alpha\)-VI\(\alpha\). Under these conditions, isomer VI\(\beta\) is converted to VI\(\alpha\) through the intermediate formation of VI\(\alpha\). The isomerization evidently proceeds through enolization of the carbonyl groups and probably may be catalyzed by the starting amines and by the resulting piperidine itself; the latter may serve as an explanation for the unusual difficulty in the isolation of samples of the \(\beta\) isomers that do not contain admixed \(\alpha\) isomers. An increase in the reaction time for diketone I with, for example, methylamine to 3 days leads to virtually only piperidine II\(\alpha\); only traces of the II\(\beta\) isomer were detected (by the thin-layer chromatography (TLC)).

In the case of the isomers of VI, their N-acetoxy derivatives (VII), which give more resolved PMR spectra, were obtained by the method in [4]. Calculation by the method in [5] of the PMR spectrum of isomer VII\(\gamma\), which is a combination of two equivalent ABK spin systems and a \(K_2M\) system (of the \(A_2B\) type), leads, with good agreement between the calculated and observed intensities of the transitions, to spin-spin coupling constants (SSCC) and chemical shifts (presented in Table 2 in parenthesis), the deviations of which from the first-order parameters are within the limits of error in recording the spectrum. For the stereochemical interpretation of the spectra one may therefore limit oneself to an examination of the first-