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REVISED STRUCTURE OF THE PRODUCT FROM ACETOPHENONE AND BENZONITRILE IN THE PRESENCE OF ALUMINUM CHLORIDE

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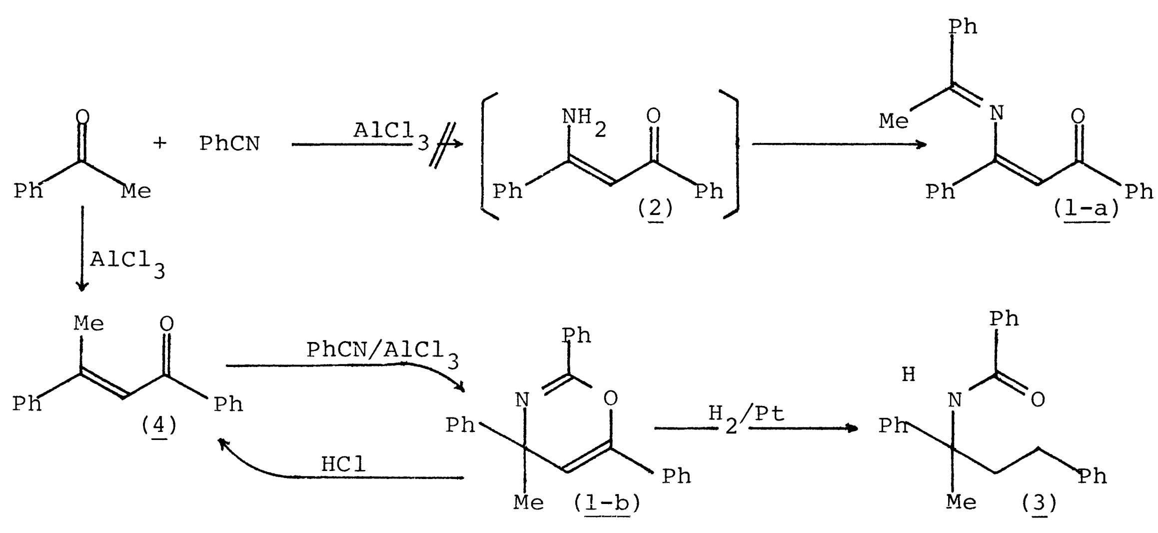
On the basis of ^{13}C-nmr and chemical studies, the title product was concluded not to be N-(1-phenylethylidene)-β-aminochalcone (1-a), as first described by Barluenga and co-workers, but 4-methyl-2,4,6-triphenyl-4H-1,3-oxazine (1-b).

In 1977, Barluenga and co-workers described$^{1)}$ that the reaction of acetophenone with benzonitrile in the presence of aluminum chloride led to the formation of compound (1) (mp 104-106°C) passing through β-aminochalcone (2). They proposed that the structure of 1 is N-(1-phenylethylidene)-β-aminochalcone (1-a) by ir, ^{1}H-nmr, and elemental analytical data. Since we have never succeeded in obtaining the Schiff bases from the reaction of the β-amino group of β-amino conjugated enones with carbonyl compounds, we reinvestigated the reaction of acetophenone with benzonitrile according to their procedures. The melting point, and ir, ^{1}H-nmr and elemental analytical data of the product were superimposed with reported data on 1. In the ^{13}C-FT-nmr spectrum of 1 in chloroform-d_1, however, two sp^3-carbon signals at δ_C 32.2 and 56.5 and three sp^2-carbon signals at δ_C 105.6, 148.6 and 150.9 appeared along with aromatic carbon signals. By the ^{1}H off-resonance decoupling technique, the signals at δ_C 32.2 and 105.6 were assigned to a methyl and a methine carbon, respectively; the other three signals except aromatic ones were due to carbon having no proton. No carbonyl carbon signal appeared in the spectrum. From these data, the structure of 1 was favored to be 4-methyl-2,4,6-triphenyl-4H-1,3-oxazine (1-b) rather than 1-a.

Leiprand and co-workers reported$^{2,3)}$ that the mixture of β-chloro ketone and



nitrile was condensed in the presence of stannic chloride to give 4H-1,3-oxazine, which was easily hydrogenated to amide. Therefore, 1 was hydrogenated in acetic acid-ethanol mixture on platinum. The ir absorption maxinum of the product appeared at 1640 and 1530 cm^{-1}, which were typical bands for benzamides. A methyl and a methylene proton signal were observed at δ_H 1.88 and 2.44 in the ^{1}H-nmr spectrum. From these spectral data and elemental analysis, the hydrogenated product was found to be N-(1-methyl-1,3-diphenylpropyl)benzamide (3). By the treatment with dilute hydrochloric acid, 1 was hydrolyzed to β-methylchalcone (4), which was identified with the authentic sample[4)] by chromatography and spectroscopy. Further, when 4 was treated with benzonitrile in the presence of aluminum chloride, the product was identical with 1.

From these facts, we concluded that the condensation product (1) from acetophenone and benzonitrile was not to be N-(1-phenylethylidene)-β-aminochalcone (1-a), but to be 4-methyl-2,4,6-triphenyl-4H-1,3-oxazine (1-b). The formation of 1-b was assumed to be the condensation of benzonitrile with β-methylchalcone (4).

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